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QUANTITATIVE
CHEMICAL ANALYSIS

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QUANTITATIVE CHEMICAL ANALYSIS

ADAPTED FOR USE IN THE LABORATORIES OF COLLEGES AND SCHOOLS

BY

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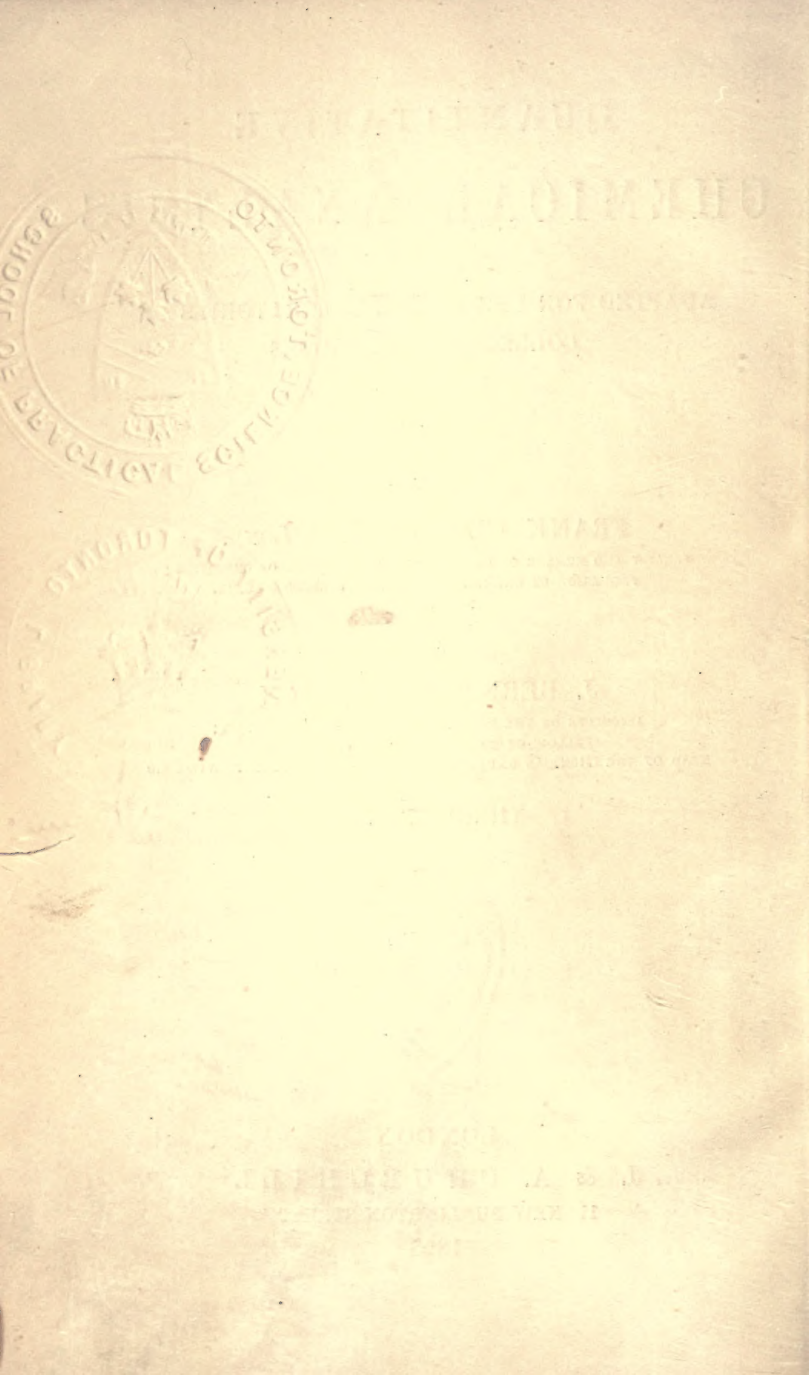

PREFACE.

THE experience derived from many years' laboratory teaching has led us to consider, that the course of Quantitative Analysis hereafter described, will be useful to chemical teachers and students, and to others.

It will be seen that the course ordinarily adopted has not been modified to any considerable extent, but an attempt has been made to introduce recent methods and apparatus.

It has also been our endeavour to make the descriptions of methods and processes as intelligible as possible. We have, accordingly, carefully introduced all necessary practical details, and have illustrated the text by numerous original engravings. The book has at the same time been kept within moderate dimensions by omitting unnecessary theoretical matter; and by inserting only typical, useful, and well-accredited methods, instead of attempting to describe all the different processes in use.

The analytical processes described in the text have been repeatedly carried out by our students in the University College, Nottingham, who have supplied the results of analyses which are inserted.

We have freely used the standard treatises, monographs, and original memoirs on the subjects treated of: and have recommended the student to refer to these sources of information, when necessary, for further details. A list of the more important works of reference will be found on pages xxi, xxii.

The book is intended to supplement rather than to replace oral instruction and demonstration by the teacher; but it is

confidently anticipated that it will in a somewhat unusual degree diminish the tutorial work of the teacher, and remove the practical difficulties of the student.

The subject-matter has been arranged in five principal Parts.

Part I. deals with the various Preliminary and General Operations which are employed in Analysis; such as the Use of the Balance, the Determination of certain Physical Constants, the Preparation of Substances for Analysis, the Ordinary Processes employed in Analysis, and the Preparation of Pure Substances; also General Rules to be observed in Working and in the Entry of Work.

Part II. is devoted to Gravimetric Analysis. A description is given of the most important Simple Gravimetric Estimations, together with others of less importance which are distinguished by being printed in smaller type. Those determinations which resemble one another have been classed together. This arrangement has been adopted in order that unnecessary repetition in description may be avoided, and the greatest convenience in reference may be secured. The analytical methods have been generally placed in the order of their increasing difficulty.

Part III. treats of Volumetric Analysis. It commences with an account of the Measuring-Vessels used for liquids, and their Calibration. A description of the preparation of Standard-Solutions follows. Various simple processes of Volumetric Estimation complete this part of the book. These are grouped in such a way as to associate those estimations which are made by means of the same solution, or which depend upon similar chemical reactions.

Part IV. contains descriptions of more Complex Quantitative Estimations. Some of these are Gravimetric, others Volumetric, and others again are mixed in their character. These processes are selected as being typical; they represent

in the main those which a student should carry out in order to get a useful knowledge of quantitative methods, for scientific and technical purposes. They include the Analysis of Ores, of various Industrial Products, of Water and Food, and of Organic Substances.

Part V. treats of Gas-Analysis. It has been restricted in its scope to the more simple methods, many of which are now commonly applied to technical purposes. The omission of the more elaborate methods has been decided upon, partly because an abstract of such processes is almost useless, and a full description would have added to the dimensions of the book somewhat seriously. Partly also because admirable accounts of these methods are at the disposal of the student in several of the standard works referred to on page 427.

The Appendix contains certain Typical Results of Analyses, in addition to those which are given in the text, also a series of Tables of Constants required for calculating the results of analyses. It concludes with Lists and particulars of the special Apparatus and Chemicals which are required for the processes referred to in the book, and with a list of the Processes of Separation contained in the text.

We have to acknowledge many valuable suggestions which have been made by Mr R. L. Whiteley during the revision of the proofs; also his contribution on the Estimation of Tannin in Tanning Materials. Dr Truman has also aided us by reviewing the portion treating on the Analysis of Milk and Butter. The numerous illustrative cuts have been engraved from photographs of the apparatus, for which we are indebted to Mr W. T. Rigby.

F. C.
J. B. C.

University College, Nottingham,
October 1891.

PREFACE TO SECOND EDITION.

THE text has undergone a complete revision for the Second Edition. It has thus, we hope, been freed from errors. The most important emendations and additions which have been made are due to the kindly interest shown by many teachers, experts, and analytical chemists, who have helped to introduce descriptions of the newer processes and forms of apparatus. We gratefully acknowledge such valuable assistance from Prof. W. A. Tilden, D.Sc., F.R.S., Prof. J. Emerson Reynolds, M.D., D.Sc., F.R.S., Messrs Otto Hehner, H. R. Procter, L. Archbutt, David Watson, D.Sc., C. A. Kohn, Ph.D., and from many others.

We have also to thank Mr R. L. Whiteley for the trouble he has taken in revising the proofs.

F. C.
J. B. C.

UNIVERSITY COLLEGE, NOTTINGHAM,
December 1893.

PREFACE TO THIRD EDITION.

THE present Edition has been improved in several respects. The book has again been enlarged, since it has been found advantageous to introduce new and improved methods of estimation. The descriptions of manipulation and of apparatus have been made clearer by revision of the text and by the insertion of additional figures. The facility of reference has also been considerably increased by reparagraphing and by the use of bold type for the paragraph headings.

We have to thank several scientific friends for carefully revising certain processes concerning which they have special knowledge, and to express our acknowledgments to Mr M. E. Feilmann, B.Sc., for carefully reading the whole of the proofs.

F. C.
J. B. C.

UNIVERSITY COLLEGE, NOTTINGHAM,
July 1895.

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BOOKS OF REFERENCE.

For General Analysis.

Fresenius' Quantitative Analysis.

For Volumetric Analysis.

Sutton's Volumetric Analysis.

For Gas Analysis.

Sutton's Volumetric Analysis.
Bunsen's Gasometrische Methode (or English edition).
Winkler's Technische Gas-analyse (or English edition).
Hempel's Gas Analysis (English translation).

For Special Analyses.

Crookes' Select Methods of Chemical Analysis.
Allen's Commercial Organic Analysis.
Hassall's Food Analysis.
Blyth's Manual of Practical Chemistry.
Frankland's Water Analysis.
Wanklyn's Water Analysis.
Wanklyn's Milk Analysis.
Hehner's and Angell's Butter Analysis.
Addyman's Agricultural Analysis.
Procter's Text-book on Tanning.
Beringer's Manual of Assaying.
Classen's Application of Electrolysis to Chemical Analysis.
Smith's Electrochemical Analysis.
Blair's Chemistry of Iron.
Lunge's Sulphuric Acid and Alkali.
Watts' Dictionary of Chemistry (First and Second Editions).

Thorpe's Dictionary of Applied Chemistry.
Groves' and Thorp's Chemical Technology.

The Journal of the Chemical Society.
The Journal of the Society of Chemical Industry.
The Chemical News.
The Analyst.

Storer's Dictionary of Solubility.

PART I.

SECTION I.

THE CHEMICAL BALANCE. WEIGHTS AND WEIGHING.

Since the operation of accurate weighing requires to be constantly carried out in quantitative analysis, it is essential that the student should become familiar with the use of the balance, which is employed for this purpose. A description of a convenient form of chemical balance, which is sufficient for all ordinary operations, is given below.

The student is referred to works on Physics for an account of the theory of the balance: the practical use of the instrument only is here described.

The Balance.

1. **The Chemical Balance** represented in fig. 1 consists essentially of a rigid beam which is supported near to and slightly above its centre of gravity. Upon either end of the beam, and equidistant from its centre, the scale-pans are suspended.

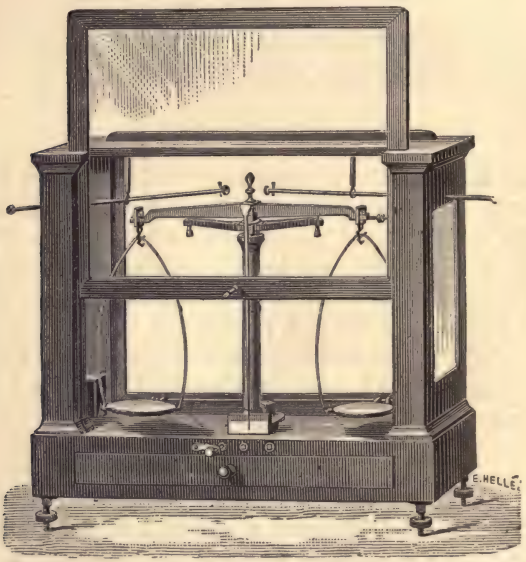
In order to diminish the friction of the working parts at each of these points of support and of suspension, the beam has let into it three knife-edges of steel, or preferably of agate, which work on agate planes. The beam and the pans (fig. 2) are supported on these edges.

When the balance is not in use, the beam is lifted from

the knife-edges, and is supported by a T-shaped rest, which is raised by rotating a disc with milled edge in the front of the balance-case. The pans also are supported, when they are not in use, by means of padded arms, which are raised by a lever in connection with a button, to the left of the milled head. The pan-rests are thrown out of action by pressing in the button and fastening it by means of a catch.

In some balances the beam and the pans are released by

FIG. 1.



one movement of the disc: this is convenient, and saves time and trouble when weighing.

Attached to the bottom of the balance-case are four set-screws which enable the balance to be adjusted to a perfectly horizontal position. The condition of true horizontal adjustment may be ascertained by the spirit-level fastened to the floor of the balance-case.

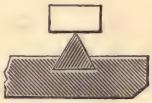
The beam of the balance is most conveniently graduated into twelve equal divisions, so as to admit of the use of a

12-milligram rider (6) for weighing fractions of milligrams. Some balance-makers, however, prefer to divide the beam of the balance into ten equal parts, and to use a 10-milligram rider.

Projecting from the right-hand end of the beam will be noticed a fine screw carrying a small brass nut, which is used for restoring equilibrium when necessary (7).

2. The Balance is inclosed in a Glass Case with equipoised sliding glass sashes at the front and back. The case shields the balance from dust, and hinders the access of acid fumes and of moisture, which rust the steel knife-edges. It also prevents air-currents from disturbing the scale-pans during weighing. The balance should be kept in a room apart from the laboratory, which is as free as possible from acid fumes and from damp, and is not subject to great changes of temperature. As a further precaution, a jar partly filled with small pieces of quicklime should stand inside the balance-case; the lime must be renewed from time to time, as it crumbles and slakes by absorbing moisture.

FIG. 2.



3. The Support on which the Balance rests must be free from vibration. Such a support may be secured by means of a slate or stone slab, resting on pillars let into the foundation of the building, and out of contact with the floor. The slab may, however, be more simply supported by brackets firmly attached to the wall: it is thus usually isolated from vibrations from the floor.

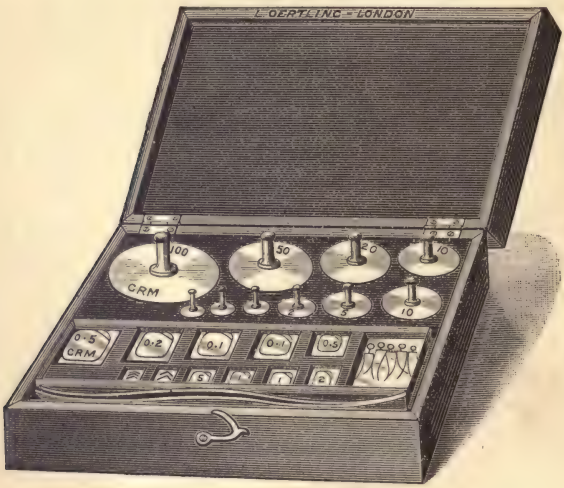
THE WEIGHTS.

4. The Weights, which are almost exclusively used by chemists, are those of the French or Metric System, in which the gram is taken as the unit. The convenience of this system is obvious; for not only is there a simple relation between the unit of weight and the units of length and

capacity; but the different denominations in weight, being related by multiples and submultiples of ten, conform to our numerical notation, and therefore render entry and chemical calculations very easy.

The weights, from one gram upwards, are usually made of brass. They are cylindrical in shape, with a handle by means of which they are lifted by a small brass forceps. The smaller weights, from 0·5 gram downwards, are made of platinum, or, better still, of aluminium foil or sheet. The low specific gravity of aluminium renders it possible to use a large volume of the metal, and therefore permits of the weights being comparatively large and thick. Aluminium weights are consequently more easily handled, and are less

FIG. 3.



liable to be bent or folded, than those of platinum. These smaller weights are square in shape, and usually have one corner turned up so as to be easily grasped by the forceps.

The weights, together with a forceps for lifting them, are usually supplied in a velvet-lined box (fig. 3). In this figure a set of weights such as are ordinarily used is represented.

The separate weights, however, differ in value in sets made by different makers, as will be seen by comparing the weights in the box with those represented in fig. 4.

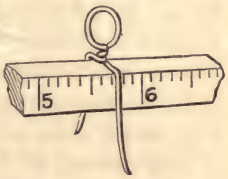
5. **The Process of Weighing is much Facilitated** by removing the weights from the box and keeping them on the front of the floor of the balance-case. They are placed on a piece of stiff cardboard (fig. 4), which is marked out into the same number of squares as there are weights. Each square is covered by a weight, the value of which has been previously written within the square. Accordingly, when the weights requisite for counterpoising any substance have been placed on the scale-pan, their value may be read off from the uncovered squares left on the card.

FIG. 4.

50	20	20	10
5	2	2	1
·5	·2	·2	·1
·05	·02	·02	·01

6. **The Rider** is a piece of wire bent as is shown in fig. 5. It is made either of gilded brass or of aluminium, and its form enables it to bestride the graduated beam of the balance, and to remain on whatever part of the beam it is placed. The rider is moved from one position to another by an arm which passes through the balance-case and is moved from the outside. Milligrams and fractions of milligrams are usually registered by means of the rider.

FIG. 5.



As has been already stated, two kinds of riders are in common use, the centigram rider and the 12-milligram rider. When the centigram rider is used, the beam of the balance is divided into ten main divisions, the space between each division being further subdivided into ten. Each main division therefore corresponds to 1 milligram, and each minor division to the tenth of a milligram.

Where the 12-milligram rider is used, the beam is divided into twelve main divisions, the intervening spaces being

divided into tenths as before. In the latter method, which is adopted in Becker's balance, the rider is easily adjusted for fractions higher than 9 milligrams and lower than 1 milligram, since the rider can be readily placed in any position between the ninth and eleventh division of the beam.

Testing and Adjustment of the Balance.

The Accuracy of the Balance should be ascertained before commencing analytical work, and after it has been properly adjusted.

7. **The Balance is Adjusted** as follows:—It is first made to assume a horizontal position by means of the levelling screws on which the case stands. As soon as the adjustment is complete, the bubble of air in the circular spirit-level will occupy the central position.

The scale-pans and the beam are then set free from their supports. A gentle oscillatory movement is usually thus imparted to the beam of the balance owing to the difference of adhesion of the two ends of the beam to their supports. The lower end of the pointer or index attached to the beam will therefore swing over several divisions of the ivory scale. If the pointer is found to oscillate through an equal number of divisions on each side of the zero of the scale, the balance is in perfect adjustment.

If the spaces described by the pointer on each side of the zero of the scale are unequal, they can be made equal by slightly turning in the right direction the nut which works on the fine screw at the right-hand end of the beam.

The observations described in paragraphs 8 and 9 are then made.

8. **Delicacy or Sensitiveness of the Balance.**—The speed of oscillation of the pointer is noted. The slower the oscillations the greater is the sensitiveness of the balance to small differences of weight, and *vice versâ*. If the sensitiveness of

the balance is great, the rate of oscillation will be unduly slow, and the operation of weighing will become tedious.

The oscillations of the pointer are slower the nearer the centre of gravity of the beam approaches the axis of its suspension. Most balances have, attached to the central portion of the beam, a screw which carries a nut. By adjusting this nut, the distance between the centre of gravity and the suspension axis of the beam can be varied at will. This will alter the sensitiveness or delicacy of the balance.

When a milligram weight is placed on one of the pans, and the beam is liberated, the pans of an ordinary balance should be thrown out of equilibrium, as indicated by the swings of the pointer. A delicate balance will be affected in this way by 0·1 milligram, but for ordinary purposes it is sufficient if the balance is sensitive to 0·2 milligram.

The delicacy of the balance may be tested by placing a milligram weight on one pan, and balancing this with the rider on the beam upon the other side. The rider is then moved gradually along the beam until a distinct deflection of the pointer is noticed, the movement of the beam being checked by the supports while the rider is being moved.

The effect of increasing the load on the pans of an ordinary balance is to slightly diminish its sensibility. But when the maximum weight which the balance can carry is placed on both pans, the addition of a milligram should have nearly the same influence upon the swings of the pointer as when the pans were empty.

9. Accuracy of Construction of the Balance.—If the weight of the same body is ascertained several times in succession, the balance should indicate equilibrium every time, if the contents of the pan remain unchanged. Faulty construction of the knife-edges will cause differences to appear in the successive weighings.

When each pan of the balance is loaded with equal weights—say, with 50 grams, and equilibrium is secured, if necessary, by the addition of small pieces of tin-foil on one pan, the equilibrium should be maintained when the loads

on the pans are exchanged. If equilibrium is not maintained when the pan-loads are exchanged, this indicates that the arms of the balance are of unequal length.

Testing the Weights.

The Weights, which are to be used in Analytical Operations, should be Tested to see that their relative values are correct. If their *relative* values are correct, it is not essential that they should possess their true *absolute* values.

10. **The Weights are Tested** in the following way:—A one-gram weight is nearly balanced with brass-clippings, and the counterpoise is then finally adjusted by the addition of small pieces of tin-foil. This weight is then replaced by another one-gram weight, when the counterpoise must still be true. The third gram weight is tested in the same way.

The two-gram weight is then balanced against two of the one-gram weights which have been already tested; the five-gram weight is tried against the two-gram and the three one-gram weights, and so on.

The fractions of the gram are then compared with one another in a similar manner, and are then finally compared with the gram weight.

If the weights are correct in relation to one another, the counterpoise in all the above cases, and in all similar cases of nominally equal values, should be absolutely true. If the weights are found to be incorrect, they should be readjusted by the maker.

The Process of Weighing.

There are two methods in common use for determining the *Apparent Weight* of a substance—the **Direct Method**, and the **Method of Substitution**. The result thus obtained must be corrected if the *Absolute Weight* is required.

11. Direct Weighing.—In this process the substance is placed upon the left-hand scale-pan, and the counterpoising weights are placed upon the right. The weight of the substance is assumed to be equal to the weights which act as a counterpoise.

This method is expeditious and is the one in common use. Its indications are correct if the balance answers satisfactorily to the tests described in paragraphs **7–9**. But if the arms of the beam are of unequal length, or if the balance is not in perfect equilibrium, the true weight of the substance is not indicated by this method. This is usually of no consequence in any one series of weighings, since the *relative weights* of the different substances and not their *true weights* are required. The relative weights will be correctly given, provided the different substances are always placed upon the same scale-pan, and the condition of the balance remains unaltered between the successive weighings of the series.

12. Weighing by Substitution gives on any balance the true weights of bodies. In this method the body is counterpoised as before. It is then removed from the scale-pan, and weights are substituted for it which are in exact equilibrium with those already placed upon the other pan. The weights thus substituted for the substance will represent the true weight of the substance, even when the balance has not previously been adjusted to equilibrium, and when the arms are not of equal length.

13. Absolute Weight.—Since the volume of the body weighed usually differs from that of the weights which counterpoise it, different volumes of air are displaced by the substance and by the weights. Hence a body which has been counterpoised by weights in air would not usually remain in equilibrium with the same weights when the balance is *in vacuo*. The difference between the weight of a body in air and its weight *in vacuo* is usually so slight that it may be neglected in ordinary analytical operations.

The absolute weight of the substance *in vacuo* can be obtained, if necessary, in the following manner:—The weight of the volume of air displaced by the weights must be subtracted from the weight of the volume of air displaced by the substance, and the number thus obtained must be added to or subtracted from the weight on the scale-pan, according as the difference is positive or negative.

Directions for Weighing.

14. The Following Rules should be attended to during the operation of weighing:—

1. After levelling the balance (7), ascertain that the scale-pans and the floor of the balance-case are perfectly clean. If necessary, carefully cleanse their surface with a large camel's-hair brush, which should be kept in the balance-case for the purpose.

2. Then gently release the pans and the beam (7), and if the beam is not caused to oscillate by its release, start its motion by gently waving the hand over one of the pans. The pointer must oscillate through equal spaces on each side of the zero of the scale (7).

This preliminary adjustment is unnecessary if the weight of the substance is obtained by difference or by substitution. Thus, supposing it is required to weigh out accurately about one gram of a powdered solid. The solid is put into a weighing bottle (fig. 6), or into some other convenient vessel, and the bottle and the substance are accurately weighed together. About a gram of the powder is then shaken out, and the vessel is again weighed. The difference between the first and second weighings will give the weight of the powder shaken out. In cases similar to this it is not necessary to attend to the previous adjustment of the beam to exact equilibrium.

3. The substance should be invariably placed on the left-hand pan, and the weights are then afterwards placed by the forceps on the right-hand pan. This insures the convenience of putting on, changing, and removing the weights by the right hand; while the beam is released from its support by the left hand.

4. The weights should be placed on the pan in systematic order. It is best to commence with a weight which is judged to be somewhat too heavy. If this is found to be the case, lower weights of the same denomination are tried in succession, until either equilibrium results or the weight is somewhat too small in amount. When this is the case

the weights of the next lower denomination should be tried in the same systematic order. This method will be found much more expeditious than that of selecting the weights at random. The milligrams and fractions of a milligram are usually ascertained by the use of the rider.

5. The approach to equipoise of the substance and the weights is judged by observing the swings of the pointer over the graduated scale. Consecutive swings to the right and to the left must finally be equal in extent.

6. The balance-case should be closed while the rider is being used; and the final observation of equilibrium must be always conducted with the case closed.

7. The weights must never be handled with the fingers, but should always be lifted with the forceps.

8. During the transfer of the weights, or the addition or removal of the body weighed, the motion of the beam and of the pans should invariably be arrested. This prevents the unnecessary wearing of the knife-edges by violent oscillation.

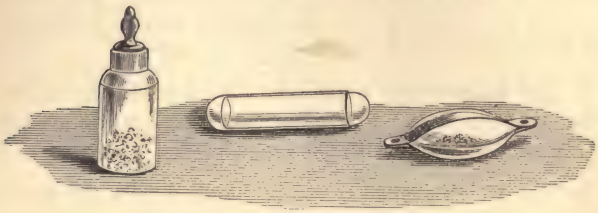
Some further conditions, which must be attended when a weighing is to be made, will be found in paragraphs **16** and **17**.

15. Entry of Weight.—As soon as a weighing is completed and an exact counterpoise has been secured, careful entry of the weight of the substance should be made in the Note-book. The best plan to secure accuracy in this entry is to write down the total value of the weights upon the pan, by noting the numbers on the uncovered spaces on the card (fig. 4, p. 5). This entry is then checked by noting the value of each weight as it is returned to its proper position on the card.

16. A Substance should not be Placed Directly on the Scale-pan, but should, as a rule, be weighed in a suitable vessel of glass, of porcelain, or of platinum. A small crucible

or evaporating basin, a clock-glass, or a watch-glass, is a suitable receptacle for a substance which is not affected by the air while it is being weighed. But hygroscopic, efflorescent, and volatile substances, and all substances which gain or lose in weight by exposure to the air, must be weighed in closed vessels, such as are represented in the following figures.

Fig. 6. Fig. 7. Fig. 8.



The ordinary stoppered weighing-bottle is seen in fig. 6. A pair of watch-glasses, ground flat at their edges, and held together by a clamp of hardened brass, are represented in fig. 8; they form a convenient receptacle for hygroscopic substances. Fig. 7 shows a pair of thin glass tubes, one of which fits closely within the other; these are commonly used for weighing dried folded filter-papers.

17. A Substance should never be Weighed while it is much Warmer or Colder than the Air in the Balance-case, else it will appear to be lighter or heavier than it should be. This is due to two causes.

Firstly, the hot body causes an ascending movement of air around it, and the air which flows in to take the place of that which has risen tends to raise the scale-pan; a body which is colder than the air, on the other hand, produces a downward air-current upon the pan, which tends to depress the pan.

Secondly, every substance tends to condense moisture from the air upon its surface; but the amount of moisture thus condensed diminishes as the temperature of the substance is higher, and increases as the temperature of the substance is lower.

A body should therefore not only be at the temperature of the air, but should have been allowed to cool in a desiccator (41) if it is to give its true weight on the balance.

EXPERIMENT I.—Carefully clean and dry the pair of watch-glasses and clamp (fig. 8), and weigh them first by the direct method, and then by the method of substitution. Register this weight in the Note-book. Cover them with a dry, clean beaker, or put them into a desiccator and reserve them for future use.

Ascertain in a similar way the weights of the bottle (fig. 6) and of the tubes (fig. 7), and carefully register these weights in the Note-book. Keep the bottle and tubes covered and clean until they are required for use.

SECTION II.

DETERMINATION OF :—
SPECIFIC GRAVITY,
MELTING-POINT,
BOILING-POINT.

In the chemical examination of substances it is frequently necessary to determine certain of their physical properties with precision. Processes for determining Specific Gravity, Melting-Point, and Boiling-Point are described in this Section. A method for ascertaining the Solubility of a substance is given in paragraph **47.**

Specific Gravity.

18. Specific Gravity may, for practical purposes, be defined as the ratio between the weights of equal volumes of two substances, one of which is taken as standard or unit. The accepted standard for solid and liquid substances is distilled water at 4° C.

Accordingly, the specific gravity of a solid or liquid is obtained by dividing the weight of the substance by the weight of an equal volume of distilled water at 4° C.

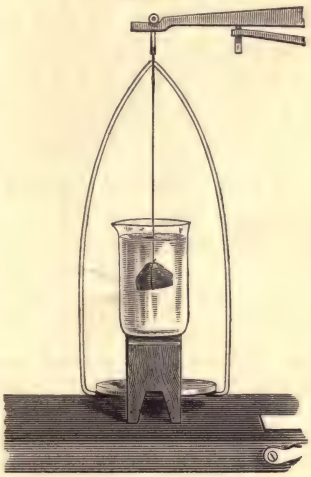
Practically it is more convenient to weigh the substance at 15°·5 C., and this temperature is therefore usually selected for taking the specific gravity.

Determination of the Specific Gravity of a Solid Substance.

19. Solid Substances Heavier than, and Insoluble in Water.—The solid is first weighed in air in the ordinary manner. It is then suspended from the beam of the balance by a fine hair or by a fibre of fine silk. The weight of the substance is now again taken while it is immersed in distilled water at 15°·5 C., care being taken that its surface is free from adherent air-bubbles.

The Removal of Air-Bubbles from the surface of a substance may generally be effected by the use of a camel's-hair brush, which is applied to the surface of the solid after it has been immersed in water. In order to remove the internal air from a porous substance, however, it is necessary to immerse the substance in boiling water for some time, or to place the vessel containing the immersed substance under the receiver of an air-pump and to exhaust the air.

Fig. 9.



A convenient arrangement for weighing the substance in water is shown in fig. 9.

A small wooden bridge is placed over the left-hand scale-pan of the balance, and on this the beaker of distilled water stands. The suspending silk-fibre is hung by a loop upon a second hook beneath the one which supports the scale-pan. The removal of the scale-pan, which would destroy the equilibrium of the balance, is thus rendered unnecessary.

The specific gravity of the solid is obtained by dividing

the weight of the body obtained in air, by the *loss* of weight which it sustains in water.

If W = Weight of solid in air,
and W_1 = Weight of solid in water,
then Sp. gr. $= \frac{W}{W - W_1}$.

Example.—In an actual experiment, a piece of brass weighed in air 16·765 grams, and in water 14·692 grams:

$$\therefore \text{Sp. gr.} = \frac{16{\cdot}765}{16{\cdot}765 - 14{\cdot}692} = \frac{16{\cdot}765}{2{\cdot}073} = 8{\cdot}088.$$

EXPERIMENT 2.—Determine the specific gravity of a crystal of Iceland spar, or of calc-spar, in the manner described.

20. Solid Substances Lighter than, and Insoluble in Water.—The solid body is weighed in air. It is then attached by means of a fine silk-thread to a solid, which is sufficiently heavy to sink the lighter body in the water. The weight of this "sinker" when immersed in water must be determined: and the weight in water of the solid with the sinker is also determined. These data will suffice for calculating the specific gravity of the solid body.

If W = Weight of the solid in air,
S = Weight of the sinker in water,
C = Combined weight of solid and sinker in water,

$$\text{then Sp. gr.} = \frac{W}{\text{loss}} = \frac{W}{W - (C - S)} = \frac{W}{W - C + S}.$$

Example.—Thus a piece of paraffin-wax was found to weigh in air 18·45 grams; the weight of the sinker in water was 49·30 grams; the combined weight of the sinker and wax in water was 47·45 grams:

$$\therefore \text{Sp. gr.} = \frac{18{\cdot}45}{18{\cdot}45 - 47{\cdot}45 + 49{\cdot}30} = \frac{18{\cdot}45}{20{\cdot}30} = 0{\cdot}909.$$

EXPERIMENT 3.—Determine the specific gravity of a piece of paraffin-wax, using as a sinker the piece of Iceland spar which was made use of in the last example.

21. Solid Substances Soluble in Water.—The solid is first weighed in air, and is then weighed in a liquid of known

specific gravity, in which it is insoluble. The specific gravity of the liquid is determined as is directed in paragraph **23**.

If W = Weight of solid in air,
W_1 = Weight of solid in the liquid,
L = Sp. gr. of the liquid.

The Sp. gr. of the solid in relation to the liquid is $\frac{W}{W - W_1}$.

But Sp. gr. of liquid : sp. gr. of water : : L : 1.

$\therefore$ Sp. gr. of solid compared with water $= \frac{W}{W - W_1} \times L$.

Example.—In an experiment a piece of loaf sugar weighed in air 6·612 grams, and in mineral naphtha (sp. gr. 0·748) its weight was 3·126 grams.

$$\therefore \text{ Sp. gr.} = \frac{6{\cdot}612}{6{\cdot}612 - 3{\cdot}126} \times 0{\cdot}748 = 1{\cdot}418.$$

EXPERIMENT 4.—Determine the specific gravity of a lump of sugar, by weighing it in air, and then in petroleum of known specific gravity.

22. Solid Substances in the state of Powder.—Occasionally it happens that the solid substance, whose specific gravity is to be determined, is in the state of powder. In such a case a bottle of known weight is taken (fig. 10, p. 19): and the weight of distilled water at 15°·5 C., which the bottle contains when exactly full, is determined (**24**).

Let the weight of this water be 50 grams.

The dry bottle containing the powdered solid is then weighed, and the weight of the solid is obtained by difference. The bottle containing the solid is then filled with distilled water at 15°·5 C., and is weighed again.

The weight of the water displaced from the bottle by the substance will be the weight of a volume of water equal to the volume of the solid. This is found by taking the difference between the weight of the solid, and the excess over 50 grams when the solid + water is weighed.

Hence, if W = Weight of solid
and W_1 = Weight of solid + water,

$$\text{Then Sp. gr.} = \frac{W}{W - (W_1 - 50)} = \frac{W}{W + 50 - W_1}.$$

Example.—In determining the specific gravity of a sample of sand, a bottle containing, when full, 50 grams of water was used. Fifteen grams of sand were poured into the empty bottle. The bottle was filled up with water, and the contents then weighed 59·6 grams;

$$\therefore \text{ Sp. gr.} = \frac{15}{15 + 50 - 59{\cdot}6} = \frac{15}{5{\cdot}4} = 2{\cdot}78.$$

EXPERIMENT 5.—Determine the specific gravity of a sample of silver sand, using a 50-gram bottle for the estimation.

SPECIFIC GRAVITY OF A LIQUID SUBSTANCE.

23. The Specific Gravity of a Liquid is usually obtained in the following manner.

An empty bottle or other suitable vessel is weighed in a perfectly clean and dry state. It is then filled with distilled water at 15°·5 C. (60° F.), and is again weighed. The difference between the two weights gives the weight of the water which the bottle contains.

The bottle is then filled with the liquid at the temperature of 15°·5 C. and is weighed again. By subtracting the weight of the vessel from this weight, the weight of a volume of liquid equal to the volume of the water is obtained. The specific gravity of the liquid is obtained by dividing the weight of the liquid by the weight of the water. Thus, if

W = Weight of vessel + water, and
W_1 = Weight of vessel + liquid, and
W_2 = Weight of vessel alone, then

$$\text{Sp. gr. of the liquid} = \frac{W_1 - W_2}{W - W_2}.$$

Two forms of apparatus are in common use for taking the specific gravity of a liquid by weighing on the balance. They are the Specific Gravity Bottle (**24**, **25**) and the Sprengel-Tube (**26**).

24. The Specific Gravity Bottle in its ordinary form is a small thin-glass bottle, into the neck of which an accurately ground perforated glass stopper is fitted. The perforation

enables the bottle to be always precisely filled with liquid, with the entire exclusion of air-bubbles. This is effected by dropping the stopper into the bottle, which has been almost filled with the liquid.

This form of specific gravity bottle is shown in fig. 10. It requires the use of a small separate thermometer for determining the temperature of the liquid.

In other forms of the bottle the stopper carries a small light thermometer, the bulb of which is immersed in the liquid in the bottle, and serves to give its temperature. Or the bottle is provided with two necks, one of which serves for the insertion of the thermometer and the other for filling in the liquid.

The bottle is thoroughly cleansed with distilled water, then dried in the steam-oven, and is weighed accurately when it is cold.

A more rapid method of drying the bottle consists in rinsing it out with alcohol, then with ether, and then placing it in the steam-oven. The process of drying by either method may be accelerated by sucking out the vapour by means of a glass tube passing down to the bottom of the bottle.

Fig. 10.

The bottle must now be filled with the standard volume of distilled water at 15°·5 C. This is most easily effected by filling the bottle with distilled water, and then immersing it in water which is several degrees above or below 15°·5 C., according to the temperature of the distilled water. If, as is usual, the temperature of the distilled water is above the standard temperature, the temperature of the water in the bath may be reduced by dissolving in it a few crystals of sodium thiosulphate or of ammonium chloride. As soon as the distilled water in the bottle shows the standard temperature by the thermometer, the stopper is carefully inserted.

The bottle is then quickly but carefully dried with a clean dry cloth, the top of the stopper being finally wiped with the dry hand, since a cloth or other porous body would absorb some of the liquid contained in the capillary bore of

the stopper. The bottle and its contents are then weighed as rapidly as possible.

The difference between the weights of the bottle, when filled and when empty, gives the weight of the water it contains. This weight must be carefully entered in the Note-book, and the weight must be redetermined from time to time, since the bottle decreases slightly in weight with use.

A precisely similar series of operations is now carried out with the liquid whose specific gravity is to be found instead of with water, and the weight of a volume of the liquid equal to that of the water is thus determined.

25. Another Form of the Specific Gravity Bottle, which is convenient for all liquids, but more especially for volatile liquids, has its neck closed with a well-fitting *solid* stopper. The neck below the stopper is considerably narrowed, and has an etched mark on it to indicate the standard capacity. This mark is some distance below the bottom of the stopper. The liquid, which has been brought to normal temperature, is filled in to the standard mark, and the stopper is at once inserted. No loss of liquid by evaporation or by expansion is then possible during the process of weighing.

Example.—In the estimation of the specific gravity of a sample of methylated spirit, a 50-gram specific gravity bottle weighed, when empty, 24·5655 grams. When filled with distilled water at 15°·5 C. it weighed 74·5445 grams; and when filled with methylated spirit at 15°·5 C. it weighed 65·9260 grams:

$$\therefore \text{Sp. gr.} = \frac{65{\cdot}9260 - 24{\cdot}5655}{74{\cdot}5445 - 24{\cdot}5655} = \frac{41{\cdot}3605}{49{\cdot}9790} = 0{\cdot}8275.$$

26. The Sprengel-Tube (fig. 11) is a light U-tube, which may replace the specific gravity bottle. The apparatus presents the advantage over the ordinary specific gravity bottle of being more readily used for taking the specific gravity of a liquid at a temperature higher than that of the atmosphere.

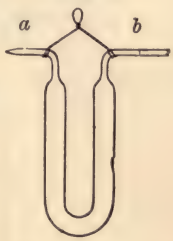
The Sprengel-tube is easily made by drawing out a piece of thin-walled glass tubing at both ends to a capillary bore. The broader portion of the tube is then bent at its middle into the form of a U, and the two capillary tubes are bent at right angles, as is shown at (*a*, *b*) in fig. 11. Close to one of the bends a mark is lightly scratched on the fine tube (*b*), and the size of the opening of the other fine tube (*a*) is

reduced by drawing it out in the flame to a tapering end and breaking off the point.

The tube is then thoroughly cleansed and dried, and the weight of the empty tube is ascertained.

The tube is next filled with distilled water by immersing the unmarked end (*a*) in water, and applying suction at the other end (*b*). The water should reach some distance beyond the mark on the tube (*b*). The tube and its contents are then brought to 15°·5 C., or to a higher temperature if necessary, by hanging the broad part of the tube in a beaker of water which is at the requisite temperature. The water should still extend beyond the mark on the narrow tube (*b*).

Fig. 11.



A piece of filter-paper is then gently pressed against the pointed extremity (*a*). The water will thus be sucked out, and as soon as the liquid exactly reaches the mark, the filter-paper is withdrawn and the tube is removed from the water, then dried and weighed.

The tube is then emptied and dried, and is filled with the liquid, whose specific gravity is required, in the way already described, and is finally weighed.

The calculation of the specific gravity is made in the same way as from the weighings with the bottle.

Example.—Thus the tube, when empty, weighed 10·5005 grams; when filled with water its weight was 16·659 grams; and when filled with petroleum-ether its weight was 14·471 grams. Accordingly, the specific gravity of petroleum-ether

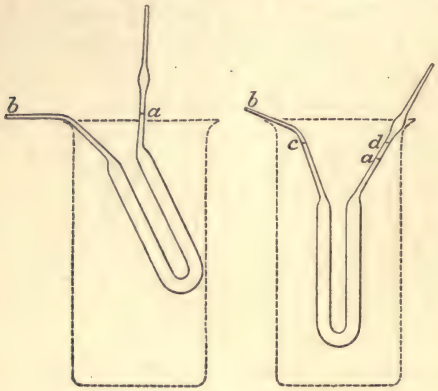
$$=\frac{14{\cdot}471-10{\cdot}5005}{16{\cdot}659-10{\cdot}5005}=\frac{3{\cdot}9705}{6{\cdot}1585}=0{\cdot}6448.$$

Experiment 6.—Determine the specific gravity of a sample of petroleum by the specific gravity bottle, and control the determination by the Sprengel-tube.

27. A Useful Modification of the Sprengel-Tube is shown in figs. 12, 13. It serves for volatile liquids and for either low or high temperatures. The narrow tubes in which the U-tube terminates are in directions at right angles to one another, but they form obtuse angles

with the limbs of the U-tube. A file-mark (*a*) is made on the capillary tube, just below the bulb, to serve for registering constant volume. The liquid is sucked in until it fills the tube and part of

FIG. 12. FIG. 13.



the bulb. It is then brought to the desired temperature. And the volume of liquid is finally adjusted by holding the apparatus with the capillary (*b*) horizontal (fig. 12), and sucking out the liquid by filter-paper applied to (*b*) until the liquid descends to the mark (*a*). When the apparatus is erect (fig. 13), the liquid sinks to (*c*) in the capillary (*b*), and ascends to (*d*) in the other capillary. The liquid is thus protected against loss by evaporation. As a further precaution the ends of the capillaries may also be covered with light glass caps. The bulb allows expansion of the liquid to take place by rise of temperature, without loss of the liquid occurring by overflow.

28. The Hydrometer enables the specific gravity of a liquid substance to be taken rapidly, since it dispenses with the process of weighing. It is a glass or metal float (fig. 14), which is weighted below, so as to cause it to assume a vertical position in the liquid. The stem is so graduated that the number which is level with the surface of the liquid, when the hydrometer is floating freely, shows the specific gravity of the liquid. The temperature of the liquid must be adjusted to the temperature required by the hydrometer, which is usually 15°·5 C.

The accuracy of the graduation may be ascertained by

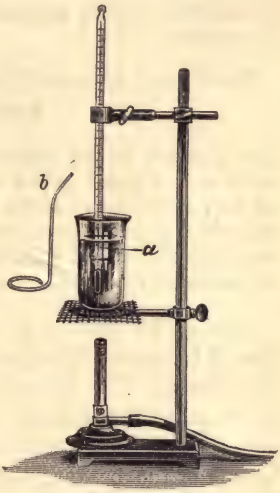
floating the hydrometer in liquids, the specific gravities of which have been determined by accurate weighing (**24–26**).

Melting-Point of a Solid Substance.

29. The Determination of the Melting-point of a Solid Substance is usually made by the apparatus shown in fig. 15.

The substance is placed in a thin-walled glass tube, which is about $\frac{1}{16}$ inch in diameter, and is sealed at one end (fig. 15).

Fig. 14. Fig. 15. Fig. 16.



Such a tube is readily made by drawing out, in the Bunsen-flame, a thin-walled, narrow test tube of about $\frac{3}{16}$ inch diameter.

This tube is attached to the stem of a delicate thermo-

meter, just above the bulb, by binding it by thread or fine wire (fig. 15); or a little rubber ring, snipped off some small rubber tubing, may be slipped over the larger end of the tube and the thermometer stem.

The thermometer and tube are next placed in a beaker containing a liquid which has a higher boiling-point than the melting-point of the solid (fig. 16). The beaker is then gently heated until the solid substance melts, and the temperature of its liquefaction is accurately noted by the thermometer.

The thermometer and tube are then removed and are allowed to cool; and the process of fusion is repeated with a fresh sample. The mean temperature obtained from several experiments made on different samples of the substance will give the melting-point of the solid.

If the Mercury Thread of the Thermometer extends above the surface of the liquid, a correction must be applied for the cooling of the mercury.

The following formula will give the correction to be added:—

$$N(T - t) \times 0{\cdot}000143.$$

Here N stands for the number of degrees on the thermometer stem which are not heated by the vapour; T is the temperature indicated by the thermometer; t is the temperature taken by placing the bulb of a second thermometer midway between the cork and the top of the mercurial column; and 0·000143 is the apparent coefficient of expansion of mercury in glass.

During the process of heating, the contents of the bath should be constantly mixed by the movement up and down of a stirrer. This is made of bent glass rod or stout wire in the shape shown at (*b*) in fig. 16. Or a slow stream of air-bubbles may be made to pass up through the liquid from the bottom of the beaker; this will efficiently mix the liquid. Continuous mixture is necessary, in order to secure a uniform temperature throughout the mass of the liquid during the determination.

The stirring may be dispensed with if the thermometer-bulb and substance are immersed in a boiling-tube contain-

ing liquid, which is itself surrounded by the liquid in the beaker or flask, which serves as the outer bath.

In the case of certain fats and of some other substances, the exact point of liquefaction is seen with difficulty. It is then preferable to use a tube open at both ends.

If any difficulty is experienced in introducing the substance into this open tube, the fine end of the tube may be inserted into the melted substance. A small quantity will enter by capillary attraction. This is allowed to cool and solidify, and the tube is then attached to the thermometer and immersed in the bath. The moment of liquefaction of the substance is indicated by its ascent in the tube. The temperature of the thermometer is noted when this movement is seen to occur.

It should be borne in mind that some substances, more especially the animal fats, show a lower melting-point when the process of fusion is repeated. In such cases the normal melting-point is regained after the substance has remained in the solid state for some time.

EXPERIMENT 7.—Determine the melting-point of a sample of paraffin-wax by both the above methods, using a beaker containing water for the bath.

BOILING-POINT OF A LIQUID SUBSTANCE.

30. The Boiling-point of a Pure Liquid is always the same under the same pressure and general conditions. This constancy of boiling-point is frequently made use of to ascertain the purity of a liquid, as well as to detect its nature.

Two methods are here described for determining the boiling-point. The first is the one commonly employed.

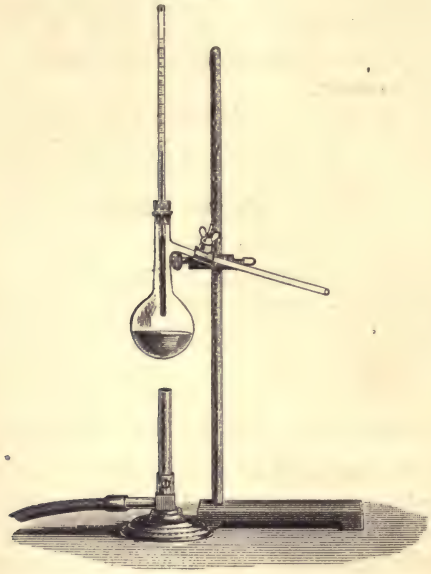
31. First Method. The liquid is placed in a flask (fig. 16), the neck of which is provided with a delivery-tube at the side. The neck is closed by a perforated cork, through which a thermometer passes. The bulb of the thermometer is just above the surface of the liquid.

Heat is gradually applied until the liquid boils, the side tube serving to carry away the vapour which is produced. The bulb and part of the stem of the thermometer are thus constantly surrounded by the vapour of the boiling liquid. If the liquid is very volatile, the neck of the flask should be attached to a Liebig's condenser.

As soon as the reading of the thermometer remains constant, the temperature is registered as the boiling-point of the liquid.

This reading will, however, require correction if the upper

FIG. 17.



part of the thread of mercury in the thermometer is cooled by extending above the cork by the formula given in par. **29**.

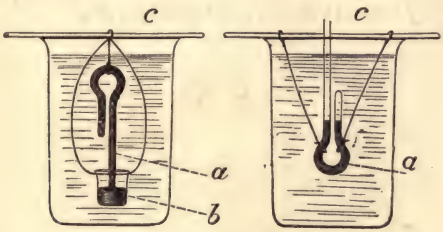
It should be remembered that considerable differences of atmospheric pressure will cause an appreciable variation in the boiling-point.

32. Second Method. A convenient method for determining the boiling-point of a liquid, especially when the quantity of liquid at

disposal is small, is described below. It depends on the fact that the pressure of the vapour of a liquid at its boiling-point is equal to the pressure of the atmosphere.

A piece of *thin-walled* glass tubing, sealed at one end, is bent in the shape of the letter U (fig. 19), the open limb being considerably longer than the closed one. A few drops of the liquid are poured into the tube, which is then inverted so that the liquid occupies the closed end. The open end is immersed in a vessel (*b*) containing mercury. A porcelain crucible or a small glass beaker may be used for this purpose. The vessel is bound to the tube, and is suspended by wire from

FIG. 18. FIG. 19.



a glass rod (*c*). The whole is then plunged into a bath and heated to a temperature higher than the boiling-point of the liquid inclosed in the tube (fig. 18). The vapour arising from the boiling liquid will expel the air from the tube.

The tube and vessel are then removed from the bath and are allowed to cool. The mercury will rise and fill the whole of the tube, with the exception only of a small space at the bend of the tube, which is occupied by the liquid, formed by the condensation of the vapour. The tube will then have the appearance shown in fig. 18. Care must be taken that no air-bubbles are present.

The tube is then carefully inverted in position, so as to cause the liquid to ascend and occupy the closed end. Mercury is now removed by pushing a glass rod down the open tube until the column of mercury is shorter in the open than in the closed limb of the tube. The tube is now ready for determining the boiling-point of the inclosed liquid.

The tube is immersed in a bath of liquid, the boiling-point of which is higher than that of the liquid in the tube, care being taken that the longer limb extends above the liquid in the bath. This is shown in fig. 19. A thermometer is then immersed in the bath with its bulb close to the closed limb of the tube, and heat is gradually applied.

As soon as the mercury columns assume the same level in both limbs, the temperature is taken. The heating is continued for a short time, and the source of heat is then removed. As soon as the mercury

in the open limb falls to the same level as that in the closed limb, the temperature is again noted. These observations are repeated several times. The mean of the temperatures thus observed gives the boiling-point of the liquid.

It is necessary to agitate the contents of the bath during the heating and cooling processes, so that the temperature may be uniform throughout the mass of the liquid. This may be effected by an appropriate stirrer (fig. 16, *b*, p. 23), or by passing a stream of air to the bottom of the vessel, and allowing the bubbles to rise through the whole height of the liquid.

EXPERIMENT 8.—Determine the boiling-point of a sample of methylated spirit by both of the above methods (**31**, **32**).

SECTION III.

MECHANICAL PREPARATION OF SOLIDS.
DRYING AND DESICCATION.
SOLUTION, EVAPORATION.
PRECIPITATION, FILTRATION.
TREATMENT OF PRECIPITATES.
PREPARATION OF PURE SUBSTANCES AND OF DOUBLE SALTS.
GENERAL RULES FOR WORKING.
ENTRY OF RESULTS.

Mechanical Preparation of Solids.

33. Before commencing the Analysis of a Substance, two conditions must usually be attended to with regard to the substance itself.

(1) The specimen chosen for analysis must be a fair and average sample of the body which is undergoing examination.

(2) The substance, if a solid, must almost invariably be in a finely-divided state.

34. Sampling.—The first condition presents no difficulty in the case of a body of homogeneous composition. But in selecting a sample of a heterogeneous mass for analysis, such, for example, as an iron ore, portions should be selected from different parts of the mass. These are then coarsely powdered and mixed, and a small quantity of this mixture is used for the analysis. Frequently a large quantity of moisture is present. In this case the sample should be selected from the interior, as the outer portions would probably be more

or less dried by exposure to the air, and would give too low a percentage of water.

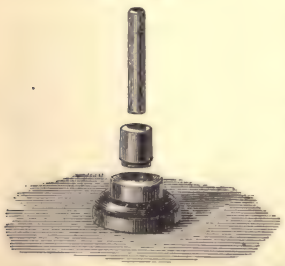
Again, in the examination of certain minerals, it will be found that the mineral of which the composition is to be ascertained, is embedded in a matrix of earthy matter, or is adherent to other minerals. Care must be taken in this case that a true sample, consisting of the desired mineral only, is detached.

35. Powdering.—The second condition, that the solid substance which is intended for analysis must be in the state of very fine powder, is also usually indispensable. In the condition of fine powder a substance is more readily acted upon by solvents and by fluxes.

The operation of powdering a substance is usually conducted in a mortar. It is essential that the mortar should be composed of harder material than the body to be powdered, or the powder will be contaminated with particles of the material of which the mortar is composed. For salts and other comparatively soft bodies, a porcelain or a Wedgwood mortar may be used; but for many minerals and other hard bodies, a mortar of steel or of agate is necessary.

When a mineral is being reduced to powder, the large pieces may be first broken by wrapping them in paper, and striking them with a hammer upon a steel anvil. The smaller pieces thus produced are then reduced to coarse powder, either in a steel mortar of the usual shape, or in a steel percussion mortar (fig. 20), which consists of a hollow cylinder fitted into a depression in the base. The substance is placed in the cavity thus formed. The solid cylindrical pestle is then pushed down upon the substance, and is struck repeatedly with a hammer until the substance is powdered.

FIG. 20.



The substance, which has been coarsely-powdered in the steel mortar, is next introduced, in small portions at a time, into an agate mortar; and the substance is further powdered by trituration, and *not by blows*, until it forms an impalpable powder. If the powder is sufficiently fine, no grittiness will be felt when it is rubbed between the thumb and finger.

To make certain that the substance is sufficiently finely powdered, it is advisable to sift it as follows:—A piece of fine muslin, which has been well washed and dried, is stretched over the mouth of a beaker and held in position by a rubber ring. The powdered substance is then put upon the muslin, and the beaker is gently tapped. The finer particles will fall through into the beaker, and the coarser pieces which remain on the muslin may then be returned to the mortar and again triturated until they pass completely through the muslin sieve. Brass sieves of various mesh are supplied by the makers, for sifting powders. Before using these, care must be taken that they are perfectly clean and dry.

Trituration with water was formerly used in the pulverisation of so-called insoluble bodies. Since, however, all solids dissolve to some extent in water, this method has been generally discarded, as it affects the composition of the substance.

Drying, or Desiccation.

36. Most Substances contain Water in varying and unknown quantity. It is frequently necessary to get rid of this water before the substance is analysed. Some of the methods of effecting this are described below, others are described hereafter.

Water may be present either as adherent water, commonly termed moisture; or as combined water, which is frequently water of crystallisation. The operation of drying is usually conducted for the purpose of removing adherent

moisture, without interfering with combined water or with any other constituent.

The removal of adherent water, or moisture, may be secured in various ways. Five methods are described below. In selecting one of these, attention must be paid to the temperature at which the substance begins to decompose, so as not to lose other constituents besides adherent moisture. Any near approach to a temperature which would cause such a change must be avoided.

37. Drying at Ordinary Temperature.—If the substance is to be superficially dried at the ordinary temperature of the air, as is usually necessary in removing the adherent mother-liquor from crystals, a convenient method of procedure is as follows.

The moist solid is placed upon a porous tile to drain. After most of the moisture has been drained off by several hours' standing, the substance is next pressed in thin layers, between folded sheets of filter-paper. These are renewed until the last sheets no longer become moist. The adherent moisture is then known to have been removed.

Another very efficient but somewhat slow method, is to expose the substance in a closed vessel called a desiccator (figs. 25, 26, pp. 37, 38) over a dish containing solid calcium chloride, strong sulphuric acid, or other absorbent of moisture. A partial vacuum in the desiccator greatly hastens this process.

38. Drying at Steam-Heat.—Substances are frequently freed from water at a temperature of 100° C. For this purpose a thin layer of the liquid or powdered substance is spread on a watch-glass, and is exposed to a gentle current of air in a steam-oven (fig. 21).

The oven is made of copper, and, with the exception of the door, it is doubly-cased throughout. The casing of the oven is filled to about three-fourths its height with water. Heat is then applied by means of a Bunsen-burner or other atmospheric burner. When the water boils, the upper part

of the hollow casing becomes filled with steam and the temperature of the interior of the oven approaches 100° C. A gentle current of air then passes through the oven, entering through an inlet near the bottom of the door, and escaping from an outlet in the top.

It has been found possible to attain a higher temperature than that usually recorded in a steam-oven, by dispensing with the usual inlet for air through the door. For this a

FIG. 21.

FIG. 22.

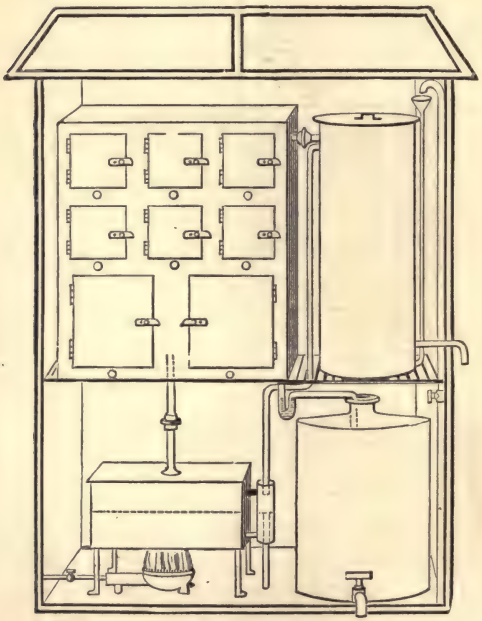
narrow copper tube is substituted, one end of which is seen immediately beneath the door, the other end opening into the oven flush with its bottom. The pipe itself is thus constantly surrounded with boiling water, and the air passing through it into the oven enters at a temperature of nearly 100°. There is a small outlet for air provided at the upper part of the back of the oven.

The arrangement for ensuring a uniform level of water in the steam-oven will be understood from the sectional drawing

(fig. 22). A constant supply of cold water flows into the vessel which is attached to the side of the steam-oven, and the excess flows away by the central tube to a sink. The water in the bath is maintained level with the top of this overflow tube by a small connecting tube below.

39. The Heating of Steam-ovens may be advantageously combined with the Distillation of Water. The apparatus suitable for this purpose stands conveniently in a recess in the laboratory wall, which is furnished with a glazed projecting hood, and with a good draught from the top. This arrangement is represented in fig. 23,

FIG. 23.



Scale one-tenth.

which is drawn to the scale of one-tenth. A copper boiler on a stand and a stoneware collecting jar are seen resting on the floor of the recess, while the set of double-cased copper ovens and the still-tub are supported on a strong iron grating above.

The steam generated by a powerful Fletcher-burner passes from the boiler through a pipe which terminates within the outer casing of the ovens, and several inches above the bottom. The steam then makes its way between and around the various ovens, undergoing partial condensation while heating them. The hot condensed water thus produced flows through a pipe, the opening of which is flush with the bottom of the oven-casing. This pipe has a U-bend to prevent the escape of steam. The water is collected in a stoneware jar, from which hot distilled water may be drawn when the apparatus is at work.

Any steam which is not condensed in heating the ovens passes from the upper part of the oven-casing into a block-tin worm inclosed in the tall still-tub. It is thus condensed, and flows as distilled water from the end of the worm-pipe into a second stoneware store-jar provided with a tap below. The level of the water inside this jar is indicated by a glass syphon-gauge.

The still-tub is supplied with a stream of cold water from a pipe, in which is a control tap. This pipe is shown at the extreme right of the figure. From the top of the opposite side of the still-tub the heated condensing-water flows into a little feeding-vessel attached to the side of the boiler, such as is shown in section in fig. 22 (p. 33). A portion of this hot water serves to keep up the water-level in the boiler to the dotted-level in the figure; and the rest flows away into the drain-pipes through a central pipe seen in the feeding-vessel.

All the connections are made by means of screw-union joints. The apparatus can, therefore, be quickly and easily disconnected and dismounted for the purpose of removing the incrustation in the boiler and on the condensing-worm, and for repairs.

This apparatus may be allowed to run uninterruptedly without any attention, after the gas-burner has been lighted and the supply of condensing-water has been regulated by the tap.

40. Drying above Steam-heat.—When a temperature higher than 100° C. is requisite for the desiccation of a substance, an air-oven (fig. 24) is usually employed. The construction of the air-oven is almost identical with that of the water-oven. Heated air, however, takes the place of boiling water and steam within the jacket. Since the bottom of the oven is usually much hotter than the air inside, the substance to be dried must not rest directly on the bottom of the oven. A pipe-clay triangle, with the wire ends turned down at right angles to the plane of the triangle, makes a convenient stand for the substance.

A thermometer passes through a cork in the top of the oven, and serves to register the temperature of the interior. Any requisite temperature can be maintained by suitably regulating the stop-cock attached to the gas-supply. It will be found that, when once the flame has been properly regulated, the temperature will remain constant for several

FIG. 24.

hours. The constant temperature is more permanent if a gas-governor is attached to the gas-supply. Gas regulators are also sold by the instrument-makers, which are very convenient when a constant temperature has to be maintained for some length of time.

The quantitative estimation of water, free and combined,

will be described in the typical analyses described further on.

41. The Desiccator.—Since many substances are hygroscopic after they have been dried, some means must be employed to prevent them from absorbing moisture from the atmosphere while they are cooling, or are waiting to be weighed. Similarly, deposition of moisture must be avoided upon dried apparatus, which is standing aside before it is weighed. The usual method of guarding such bodies against atmospheric moisture is to inclose them in an air-tight vessel, the air in which is kept dry by exposure to a desiccating agent. Either sulphuric acid or calcium chloride is the drying reagent commonly used. Two forms of this drying-vessel or desiccator are in common use.

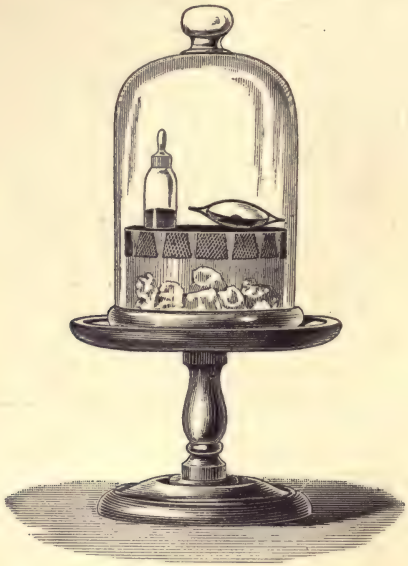
A small and portable form of desiccator (fig. 25) is usually employed, because it is easily carried from the working-bench to the balance. It consists of a broad glass jar which is con-

FIG. 25.

tracted in the middle. The lower portion contains the desiccating agent; the upper portion incloses the body to be weighed. A circular piece of perforated zinc forms a bottom to the upper chamber, and on this a pipe-clay triangle or other support is laid. The body to be cooled and weighed is placed on this support. A flat lid is ground to fit accurately on

the upper ground rim of the desiccator; and this rim is lightly greased with lard, so that the lid may fit air-tight.

FIG. 26.



Thus an air-tight chamber is formed in which a body may cool in dry air and be kept from contact with moisture.

Another larger form of desiccator, which may be conveniently kept in the balance-room, is shown in fig. 26.

SOLUTION OF SOLIDS.

42. The Process of Solution of a solid substance usually precedes the process of analysis. Several methods of performing this operation are described in this Section.

In most cases it is essential that the solid substance to be dissolved should be in a fine state of division. It is powdered, if necessary, as was described in paragraph **35**.

43. If the Substance is Soluble in Water, a convenient method of dissolving it is shown in fig. 27. The substance is mixed with distilled water in a beaker, which is then placed on wire-gauze over a Bunsen-flame. If the heating of the contents of the beaker causes bumping, the water and powder should be stirred occasionally with a glass rod. In order to prevent loss by spirting, the beaker is covered with a clock-glass.

FIG. 27.

44. If the Substance Dissolves with Effervescence, as is frequently the case during solution in acids, the following methods are preferable :—

(a). The solid is placed in a conical flask. The solvent is next added through a small glass funnel, which is left in the mouth of the flask and serves to partially close it during solution, as is shown in fig. 28. This will prevent loss of the solution by spirting, but will allow the escape of gas.

(b). Or the substance may be placed in a round flask, tilted at an angle of about 45°, as is shown in fig. 29. In this case also the drops thrown up by effervescence will be retained by striking the inside of the flask, while gas will freely escape.

45. Insoluble Substances. The description of the process of treating a substance which is insoluble in water and in acids will be found under paragraph **97.**

46. Material of Vessels. Care must be exercised in selecting vessels which will not be acted upon by the solvent during the processes of solution and evaporation. Thus glass

and porcelain, and in certain cases platinum vessels, may be used for acid liquids. Porcelain, silver, and nickel vessels

Fig. 28.

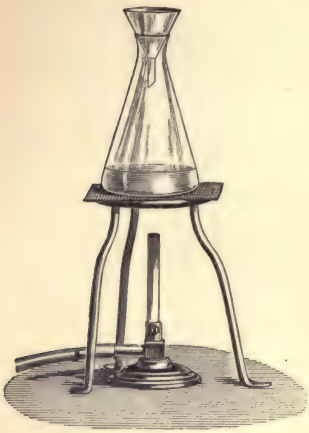
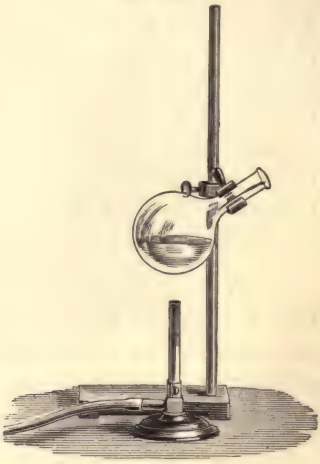


Fig. 29.



may be used for alkaline liquids: glass vessels are less suitable, since glass is appreciably acted on by alkaline liquids.

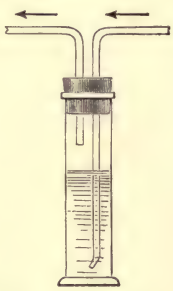
Solubility of Solids.

47. The Solubility of a Substance may usually be readily determined by means of the following simple apparatus.

A glass cylinder of about 250 c.c. capacity is selected. The mouth is closed with an india-rubber cork, in which two holes have been bored. In one of the holes is fitted a short piece of glass tube bent at right angles, the tube just passing through the cork (fig. 30). Through the other hole passes a piece of glass tube, also bent at right angles, and long enough to reach the bottom of the cylinder. The lower end of this tube is slightly contracted and is bent obliquely.

The cylinder is about two-thirds filled with distilled water. It is then immersed up to the level of the liquid surface, in a large vessel containing water. This water must be maintained at the temperature which has been selected for determining the solubility of the substance. The coarsely-powdered solid is then introduced into the cylinder in quantity more than would be sufficient to form a saturated solution.

Fig. 30.



The rubber stopper is then inserted, and the end of the shorter tube is connected by rubber tubing with the high-pressure water-aspirator (fig. 42, p. 56). The stream of air-bubbles which is thus drawn through the liquid causes the solid and the water in the cylinder to constantly circulate. In from 15 to 30 minutes a saturated solution of the solid will be formed.

Some of the clear solution may then be weighed in a stoppered vessel (fig. 6, p. 12), and the amount of solid matter dissolved in it may be estimated either by evaporation or by precipitation, according to the nature of the substance.

The insertion of a plug of cotton-wool into the end of the longer tube will serve to filter off the dust of the air, and to prevent it from being introduced into the liquid. Supersaturation of the solution may arise from the evaporation caused by the passage of the air through the solution. This may be prevented by allowing the air to bubble through water on its way to the cylinder, so that it becomes saturated with moisture.

If high-pressure water cannot be obtained, steam from a boiling flask of water may be blown through the aspirator (Fig. 42), and will produce a satisfactory result. Or a special form of apparatus for producing aspiration (**141**) may be used.

If the solid to be dissolved would undergo chemical change

by exposure to oxygen, a stream of coal-gas or other inert gas may be substituted for the air current. If coal-gas is used, it may be drawn from the ordinary service-pipes; it should be freed from oxygen by passing through at least three 9-inch U-tubes filled with pumice soaked in alkaline pyrogallate solution. This solution is made by dissolving 10 grams of pyrogallic acid in 100 c.c. of potassium hydrate solution of 1·2 specific gravity.

Example.—The following calculation of solubility from the results of an experiment will serve to illustrate the process of calculation :—

	gram.
Weight of solution + bottle,	31·8910
Weight of bottle, . .	16·2655
Weight of solution, .	15·6255
Weight of solid + dish, .	22·5100
Weight of dish, . . .	21·6110
	0·8990

Accordingly 0·8990 gram of salt is dissolved in 15·6255 − 0·8990 = 14·7265 grams of water.

Therefore, the weight of salt dissolved in 100 parts of water, ... = $\frac{0{\cdot}899 \times 100}{14{\cdot}7265} = 6{\cdot}104$

Experiment 9.—Weigh out roughly 30 grams of $KClO_3$, and pour this into a cylinder fitted as is described above. Add water and pass the current of air for half an hour. Filter off the liquid through a dry filter-paper, rejecting the first portion of the filtrate, which is partially deprived of its salt by the action of the filter-paper.

Then allow about 20 c.c. of the solution to pass into a weighed weighing-bottle (fig. 6, p. 12). Insert the stopper, and weigh the bottle and solution.

Then pour the solution from the bottle into a weighed porcelain dish, and rinse the bottle into the dish several times with distilled water. Evaporate this liquid to dryness over the water-bath (49). Then place the dish in the steam-oven (38) for about twenty minutes; allow it to cool in the desiccator, and weigh it.

The first weighing, less the weight of the bottle, will give the weight of the solid + water. The second weighing, less the weight of the dish, will give the weight of the solid dissolved. Hence the necessary data are obtained for calculating the percentage of the solid present in the solution, when it is saturated at the temperature of the experiment.

EXPERIMENT 10.—The solubility of crystallised copper sulphate, $CuSO_4.5H_2O$, may be estimated by precipitation. In this case, proceed as in the previous experiment to make a saturated solution. Since, however, crystallised copper sulphate loses a part only of its water of crystallisation when it is dried at 100°, the true weight of the salt in solution cannot be obtained by evaporating the weighed solution, and then drying the residue and weighing it, as in the case of $KClO_3$. After accurately weighing about 5 c.c. of the $CuSO_4$ solution, the Cu should therefore be completely precipitated and weighed, as is described in the estimation of Cu as CuO (90). From the weight of CuO thus obtained, the weight of $CuSO_4.5H_2O$ in solution can be calculated.

EVAPORATION.

The Process of Evaporation serves either to concentrate a solution, or to totally expel the liquid from it, and is usually effected by means of heat. A liquid is generally evaporated in a basin made of porcelain, platinum, nickel, or silver. Occasionally a beaker or crucible is used.

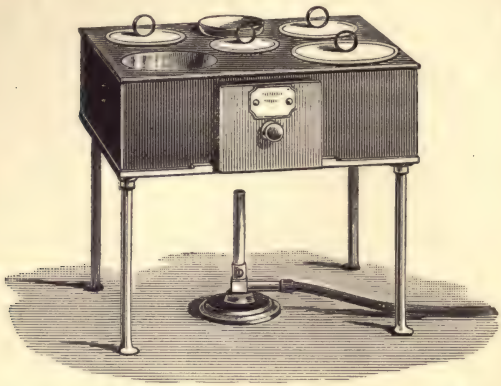
FIG. 31.

48. Evaporation at Steam-heat.—The evaporation of a liquid is frequently conducted over boiling water upon a water-bath: steam being in this case the heating agent.

A simple form of water-bath is shown in fig. 31. It consists of a copper vessel rather more than half-filled with water, and heated by a Bunsen-burner. The upper portion can be fitted with flat sheet-copper rings of gradually diminishing diameters: and thus the top of the bath can be made to support vessels of various sizes.

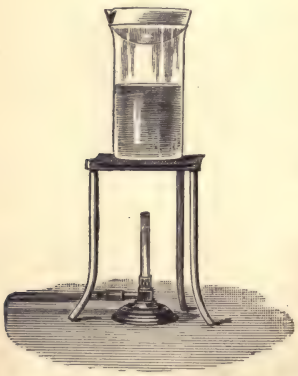
A more complex form of water-bath is shown in fig. 32. In the upper surface of this bath there are holes of various

Fig. 32.



sizes, designed to fit vessels of different dimensions. These holes, when not in use, are covered by lids as is shown in the figure. This water-bath may be fitted with a constant water supply, such as that represented in fig. 22 (p. 33).

Fig. 33.



When the vessel, in which the evaporation is conducted on a copper water-bath, is to be afterwards weighed, it should rest on a glass ring, since contact with the copper edge is apt to stain it. The upper part of a beaker of suitable diameter makes an excellent support for this purpose. A beaker, the lower part of which has been cracked or broken, may readily be converted into such a ring-support, by leading a crack round it about an inch below the upper edge, by means of a hot wire.

49. A Simple Water-bath may be improvised from a beaker partially filled with water and heated over a Bunsen-burner (fig. 33). A few

small pieces of paper thrown into the water will prevent it from bumping during the boiling. The dish placed on the top of the beaker will rarely fit it so as to be steam-tight: if this should be the case, some strips of paper may be inserted.

50. Evaporation at Temperatures above Steam-heat.—When a temperature higher than 100° C. is required for evaporation, one of the following methods may be used.

(a). *Sand-bath.*—The vessel containing the liquid may be placed on a sand-bath which is heated by a burner. The

FIG. 34.

sand-bath is a shallow sheet-iron saucer filled with silver sand. A uniform heat can be applied to the bottom of the vessel, by immersing it to the depth of an inch or less in the sand.

(b). *Naked Flame.*—The vessel may be heated directly by a naked flame, using preferably a rose-burner for large vessels. The hot air arising from an Argand-burner of the Wallace form (p. 62) also answers well.

(c). *Wire-gauze, Asbestos, or Iron-plate as support.*—The vessel may be supported on wire-gauze, or on a sheet of asbestos mill-board, or on an iron-plate. This last support is

shown in fig. 34. It is convenient for evaporating a liquid in a beaker, since the rate of evaporation can be reduced by removing the beaker to a greater distance from the part of the plate which is directly over the flame.

(d). *Air-bath.*—Beakers may be conveniently heated in a copper air-bath. The bath is similar to the water-bath represented in fig. 32, but is deeper. The beakers are supported by their curved-over edges in the holes in the top of the bath, the holes being reduced, if necessary, by means of flat copper rings. The beakers are thus immersed in the hot air inside the bath, and are exposed to a uniform temperature, which can be ascertained and regulated by means of a thermometer, the bulb of which is situated halfway down the bath. The air-bath may be employed not only for evaporating solutions in beakers to dryness, but also for drying the residue which is left on evaporation.

FIG. 35.

(e). *Loss by Effervescence.*—If effervescence occurs during evaporation, a tilted flask (fig. 29, p. 40) may be used to avoid loss by spirting. Another plan is to use an evaporating dish, and to cover it with a large inverted funnel, as is shown in fig. 35.

51. The Following Precautions should be observed during Evaporation:—

(a). Vigorous ebullition must not be allowed to take place in an open vessel, as this would lead to loss of substance by spirting. Precautions have been already described which prevent the occurrence of loss from a boiling liquid (44).

(b). When the evaporation of a solution takes place over a naked flame or over a sand-bath, the vessel should, if possible, be transferred to a water-bath towards the end of the process. This is advisable, because when a liquid is rendered thick and pasty by the separation of solid matter, it is apt to spirt considerably, even when it is heated below its boiling-point.

(c). Frequently the liquid creeps up the sides of the vessel during evaporation. This is particularly the case with solutions containing ammonium salts. The evaporation in these cases should be carefully watched, and the incrustation which forms near the edge of the vessel should be detached and pushed down by means of a glass rod. If the inner edge of the vessel is lightly greased, the ascent of the liquid will be prevented. If the liquid is heated from above, the ascent of the solution may also be prevented : an example is afforded in the estimation of Na as Na_2SO_4 (135).

Precipitation from Solution.

52. Precipitation serves to convert a substance which is in solution into an insoluble form. A substance is precipitated in order to obtain it in a form in which it may be collected and weighed. The process is also applied to effect the separation of bodies from one another.

Precipitation is usually performed in a glass beaker; but if strongly alkaline liquids are used, which would attack glass, a porcelain vessel is preferable.

Precipitation is usually effected in hot liquids. If the solution is boiling, it should be contained in a beaker covered with a clock-glass, or in a flask inclined at a suitable angle, so as to prevent loss by spirting (43, 44). After the addition of the precipitant the liquid is well stirred, and is usually allowed to stand for some time, to insure complete precipi-

tation. The formation of the precipitate in a granular condition tends to facilitate filtration.

Some precipitates form rapidly, and being flocculent may be filtered off at once. $Fe_2(HO)_6$ and $Al_2(HO)_6$ are of this description.

Agitation frequently assists precipitation. For instance, Mg, when precipitated as $MgNH_4PO_4.6H_2O$, will take several hours for complete precipitation under ordinary conditions, whereas violent agitation will insure complete precipitation in the course of a few minutes.

In most cases of precipitation, the addition of a *large* excess of the precipitant should be avoided, but the presence of a slight excess is requisite to insure the completion of the process.

The presence of excess of the precipitant should be always proved. This is usually effected by adding a few drops of the precipitant solution to the clear liquid from which the precipitate has subsided. The clear filtrate should be subsequently tested in the same way as a safeguard. In neither case must any further precipitation occur.

When a liquid is to be transferred from one vessel to another, that part of the outside edge of the vessel over which the liquid will be poured should be slightly greased with lard. The liquid should then be poured down a wet glass rod pressed against the edge of the upper vessel, as is shown in fig. 36. These precautions prevent the liquid from running down the outside of the vessel, and from splashing. For the same reason the lower end of the rod should touch the inside of a beaker into which the liquid is being poured.

EXPERIMENT 11.—Partially fill a weighing-bottle (fig. 6, p. 12) with pure recrystallised potash alum, $AlK(SO_4)_2.12H_2O$, in a powdered condition. Carefully weigh the bottle. Then shake out about 1 gram of the salt into a sixteen-ounce beaker, and carefully weigh the bottle again. The difference between the two weighings will give the weight of the salt transferred to the beaker.

Dissolve this salt in about 150 c.c. of distilled water, which contains a little dilute HCl; add some AmCl solution to cause the precipitate to form subsequently in a granular condition, and heat the contents of the covered beaker to boiling. Then heat about 50 c.c. of $BaCl_2$ solution to boiling, and add the greater part of this to the contents of the beaker. A granular white precipitate of $BaSO_4$ will form, and will quickly subside.

More $BaCl_2$ solution should be dropped into the clear liquid, to see if the precipitation is complete. As soon as this is the case, the covered beaker and its contents may be put by for further use.

EXPERIMENT 12. — Weigh accurately about 2 grams of $AlK(SO_4)_2.12H_2O$ into a sixteen-ounce beaker. Dissolve the salt in water, heat the solution to boiling, and add AmHO solution in *slight* excess. A white gelatinous precipitate of $Al_2(HO)_6$ will form. Boil the liquid until the smell of ammonia has almost entirely disappeared, then put by the covered beaker with its contents.

FILTRATION AND WASHING OF PRECIPITATES.

53. A precipitate is separated from the liquid in which it has been formed, by filtering the latter through a specially prepared filter-paper.

The filter-paper should contain the least possible weight of mineral matter or ash. The best quantitative filter-paper, when purchased, has already been treated with hydrochloric and hydrofluoric acids and then thoroughly washed to remove mineral matter. When a 4½-inch filter, cut from such paper, is burnt, it will not leave more than 1 milligram of ash.

If a precipitate is heavy and settles quickly, most of the supernatant liquid may be removed by decantation; the liquid being poured off through the filter-paper without disturbing the precipitate (fig. 36).

Usually the operations of filtration and decantation are combined in the following manner:—After the liquid has been decanted through the filter, a fresh quantity of distilled water, or other washing liquid, is poured upon the precipitate, and the contents of the beaker are stirred or boiled. The

precipitate is then allowed to subside, and the clear liquid is decanted off through the same filter. These operations are repeated several times. Finally the precipitate is transferred to the filter-paper by means of the fine stream from the wash-bottle; the removal of the precipitate being assisted, if necessary, by the use of a glass rod, tipped with about 1 inch of tightly-fitting smooth india-rubber tubing. The washing of the precipitate on the filter is then finished with a wash-bottle.

Fig. 36.

If it is found impossible to remove the precipitate from the beaker by the glass rod, it may usually be dissolved and reprecipitated.

The filter-paper must fit closely to the funnel, and the overlapping parts of the paper must be pressed together by the finger so that the precipitate cannot get between them.

The end of the stem of the funnel should touch the side of the vessel into which the filtrate passes. This not only prevents splashing, but hastens filtration.

A convenient form of wash-bottle is shown in fig. 37. It consists of an eighteen-ounce conical flask fitted with an india-rubber cork and tubes in the ordinary way. The jet,

however, is movable, since it is attached by india-rubber tubing. This enables the stream of liquid to be projected in any direction.

When Boiling Water or a Liquid which gives off Vapour or Gas is used in the wash-bottle, a special stopper, shown in fig. 38, should be used, to prevent the gas or vapour from entering the mouth.

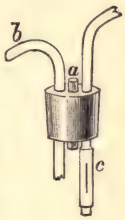
The stopper is perforated with three holes. Through the centre hole is pushed a short glass tube (*a*) which terminates just above and just below the stopper.

The other holes carry the jet (*b*) and blow-tube (*c*), as in the ordinary bottle. The lower end of the blow-tube, however, is fitted with a valve by slipping over it a piece of rubber tube, which is closed by a piece of glass rod, and has a slit cut in it as is shown at *c*.

Fig. 37.

While the wash-bottle is being used the tube (*a*) is closed by the finger, and air is blown in through the valve (*c*). The valve (*c*) prevents the air from returning through the blow-tube, and no vapour or gas can therefore make its way into the mouth. As soon as the washing is finished, the finger is removed from (*a*) and the stream of liquid is thus at once stopped.

Fig. 38.



54. The Following Precautions should be observed while the precipitate is being washed on the filter-paper :—

The precipitate should never more than half fill the filter-paper.

The washing liquid should be allowed to drain away completely from the filter before a fresh portion is added.

The liquid should never fill the filter; but the upper edge of the filter must be carefully washed with the stream from the bottle.

If the washing liquid is distilled water, it should be used hot when permissible, as hot water passes through the filter more rapidly than cold water does.

In all cases the final washing-water from the filter should be tested to prove that all soluble matter has been removed. This may be ascertained by evaporating a few drops of the water to dryness on a thin watch-glass, and seeing if there is any residue; or a delicate test may be applied for a substance which is being removed by the washing process.

EXPERIMENT 13.—The precipitate of $BaSO_4$ (52, Exp. 11) may be washed by pouring off the supernatant liquid through the filter, taking care that no precipitate is poured off with the liquid. The precipitate is then stirred up and boiled three times in succession with fresh portions of boiling water, the precipitate being allowed to subside after each addition of water, and the supernatant liquid being poured off through the filter-paper.

Finally the precipitate is transferred to the filter in the manner already described. The washing is then continued on the filter, until the addition of $AgNO_3$ solution to the last few drops of the washing-water no longer gives any turbidity. This precipitate is reserved for the further treatment which is described in Exp. 17 (78).

ACCELERATED FILTRATION.

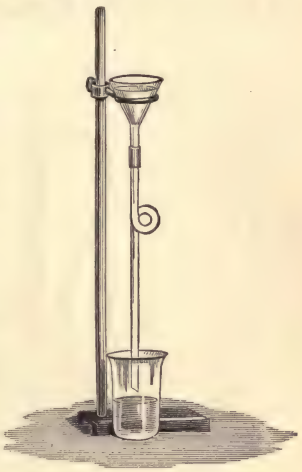
It is often desirable to hasten the process of filtration and washing. This is especially the case when a flocculent precipitate is being dealt with.

55. Acceleration by Lengthened Funnel-tube.—One of the simplest means of increasing the rate of filtration is to attach to the funnel a glass tube, bent as is shown in fig. 39. As soon as the filtrate has filled the tube, the weight of the column of liquid tends to draw the liquid through the filter, and the rate of filtration is accordingly increased.

Another simple method is to attach to the funnel a *straight* piece of glass tube about 2 feet in length and 1 millimetre in bore. The liquid passes down the tube in a nearly unbroken column, the weight of which tends to draw the liquid through the paper.

56. Acceleration by Filter-pump.—The most rapid filtration, however, is secured by removing the atmospheric pressure from beneath the filter more or less completely. The full atmospheric pressure, being still exerted on the surface of the liquid in the funnel, forces the liquid through the filter.

Fig. 39.



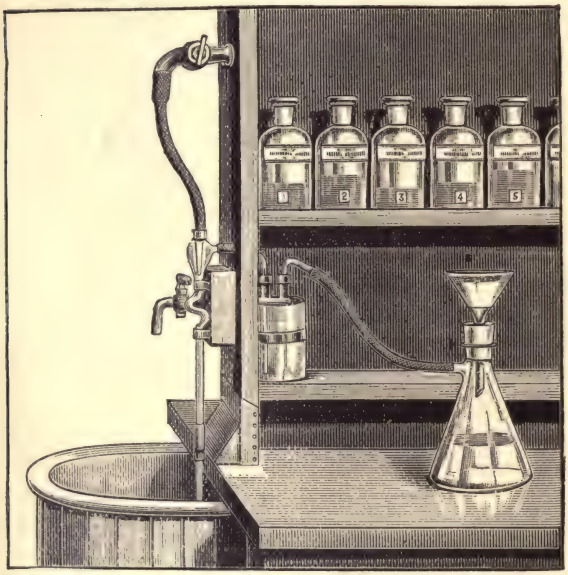
The pressure thus brought to bear on the filter-paper is usually greater than the ordinary paper in the wet condition can support. It becomes necessary, therefore, either to use specially prepared toughened filter-paper, or to support the ordinary paper in a suitable way (57), so as to enable it to withstand the pressure.

The filter-paper is fitted as follows:—A funnel is selected, the sides of which inclose an angle of 60°. The muslin or the platinum cone (57 b, c) is placed in the funnel; and then a dry filter-paper, folded in the ordinary manner, is inserted. The filter-paper is pressed with the finger until the supporting muslin or platinum and the paper fit the sides of the funnel closely: and while it is thus held in position, the filter is wetted by pouring in a little distilled water. The overlapping edges of the filter-paper are pressed down by the finger, and any air-bubbles between the funnel and the paper are also carefully removed by pressure.

The funnel is then fitted by means of a perforated rubber stopper into the neck of a clean, strong, conical filtering-flask, of about 24 ounces capacity. The flask is placed in connection with an exhausting syringe, or better with a suitable water-aspirator (58), by means of the side-tube in its neck (fig. 40).

Before the filtration is started, it is well to fill the filter with distilled water and to start the pump, in order to ascertain that everything is in working order. If any air is seen to be sucked down between the filter and the funnel, this may be stopped by gently pressing the moistened edges of the paper against the funnel.

Fig. 40.



The aspirator should be started gently, since the particles of some precipitates may be easily drawn through the paper at first.

During the filtration and washing, liquid should be constantly poured into the filter, so that it is never quite empty; otherwise fissures are apt to form in the mass of the precipitate. If this should occur, efficient washing becomes impossible, since the water ceases to pass through the mass of the precipitate.

The operation of washing gelatinous precipitates is very

much shortened when the pump is employed; moreover, if air is drawn through the precipitate for a few minutes after the washing-water has run through, the time required for drying the precipitate in the steam-oven is considerably lessened.

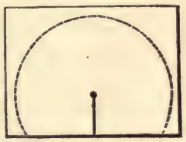
57. Special Filter-paper, and Supports for the Filter, are described below, for use when the filter-pump is employed.

(a). *Thin Toughened Filter-papers* can now be obtained, which well satisfactorily withstand the atmospheric pressure when it is brought to bear on them. Messrs Schleicher and Schüll's No. 575 paper is perfectly satisfactory for this purpose.

(b). *Toughened Paper, or Muslin Support.*—If ordinary untoughened filter-paper is used, it may be most simply supported at the conical point by means of a small toughened paper cone or filter dropped into the funnel.

Or a small circular piece of muslin may be folded like a filter and placed in the funnel, and the filter-paper is then folded and pushed into position over the muslin.

FIG. 41.



(c). *Platinum Cone Support.*—The apex of the untoughened filter may also be supported by a platinum cone. To prepare this, a piece of platinum foil, 1½ inches long by 1¼ inches broad, is pierced a little below its middle point by a pin. A cut is made from the middle of the longer edge to this hole. The corners are then removed by cutting with scissors round the segment of an inscribed circle, whose centre is the pin-hole, as is shown by the dotted line in fig. 41. The foil is annealed by being heated to redness; it is then folded into a cone with the pin-hole as an apex, and is adjusted to fit into the funnel.

58. The Geissler Water-aspirator.—A convenient form of water-aspirator or filter-pump is that invented by Geissler (fig. 42). It is shown in fig. 40 attached to a high-pressure water-supply by means of stout india-rubber tubing: this tubing should have strong canvas inserted in its walls to enable it to withstand the pressure of the water. The rubber tubing should be firmly bound with copper bell-wire to the water-tap and to the aspirator.

This aspirator has three tubes fused into the chamber in the upper part. The upper vertical tube conveys the water, which passes through the contracted end of this tube into the opening immediately below it. During its passage the water draws air from the chamber and carries it away through the lower vertical outlet tube. Air is thus drawn through the side horizontal tube; and any vessel

which is placed in connection with this tube will consequently be gradually exhausted of its air.

The side-tube of the filter-pump is connected with a tube which passes to the bottom of a small two-necked bottle (fig. 40). The other tube of this bottle passes just through the cork in the second neck, and is connected by rubber tubing with the side-tube of the filtering-flask.

FIG. 42.

The two-necked bottle serves to prevent any tap-water from the aspirator from finding its way back into the filtering-flask. When the water-supply is suddenly checked, the water from the aspirator is drawn back through the side-tube by the partial vacuum; but instead of entering the filtering-flask, it is received by the two-necked bottle. The water is thus prevented from mixing with the filtrate in the flask. As soon as the pump is again started, the water in the bottle is rapidly sucked out.

A current of steam from a vessel of boiling water may be blown down the top tube of the aspirator, instead of using high-pressure water, as is shown in the figure.

EXPERIMENT 14.—Transfer the liquid containing the precipitate of $Al_2(HO)_6$ (52, Exp. 12) to a filter-paper fitted into a funnel which is connected with the filter-pump. Wash with successive quantities of hot water, until the washing-water as it leaves the funnel no longer turns turmeric-paper brown. Afterwards continue the washing, until the last few drops of the washing-water give no precipitate on being boiled with $BaCl_2$ solution and allowed to stand for a few minutes. Reserve this precipitate for further treatment.

DRYING PRECIPITATES.

59. The next process in the preparation of a precipitate for weighing is that of drying.

Occasionally the precipitate and paper must be dried thoroughly at a temperature of 100°–110° C., and weighed: the weight of the dried filter-paper having been first ascertained.

In most cases, however, this method may be replaced by one of greater accuracy and rapidity of execution. This consists in drying the precipitate in a filter of unknown weight, which furnishes, when burnt, an ash of known weight. The dry filter is in this case burnt, and the ignited precipitate is weighed together with the ash of the filter.

60. When the Filter is to be Burnt, it is dried as follows :—The funnel containing the filter and precipitate is covered loosely with a filter-paper, so as to exclude dust, and is then supported in a truncated tin cone (fig. 43) or other suitable stand in the steam-oven (fig. 21, p. 33). The cone allows the heated air to circulate freely around the funnel, and to heat and dry the filter and precipitate.

FIG. 43.

EXPERIMENT 15.—The precipitates of $BaSO_4$ and of $Al_2(HO)_6$, which were washed as was described in Experiments 13 and 14 (pp. 52, 56), are dried in the above manner.

61. When the Filter and Precipitate are to be Dried at a Temperature not exceeding 110° C., and then Weighed without further Treatment, as in the estimation of potassium in the form of K_2PtCl (**136**), the following is the usual method of procedure. Another method is also described.

If the precipitate requires to be dried at 100° C., the steam-oven (fig. 21, p. 33) may be used. If a temperature higher than 100° C. is requisite, the air-oven (fig. 24, p. 36) is substituted: but in this case the temperature must not exceed 110° C., or the paper will be charred.

In all cases the weight of the dried filter about to be used in the filtration must first be ascertained. If any liquid which will pass through the filter-paper is likely to extract any constituent from it, the paper should first be treated with this liquid. Paper already prepared in this way can usually be bought.

In order to dry the filter, it is folded and placed either in one of the filter-tubes (fig. 7, p. 12), or upon one of the watch-glasses with clip (fig. 8). The filter-tube or watch-glass, containing the filter-paper, may then be placed on the floor of the steam-oven. If the air-oven is used, the filter-tube or watch-glass should be placed on a tripod, made of a pipe-clay triangle or other non-conducting material, and must not rest on the floor of the oven. If this is not attended to,

the temperature of the filter may become much higher than that registered by the thermometer inside the air-oven, since the heat will be conducted directly from the hot floor of the oven to the glass and filter. The filter would then become charred.

After the filter-paper has been in the oven for about an hour, it is taken out and quickly inclosed in the tube by pushing over it the second tube, or it is clamped between the watch-glasses. It is then allowed to cool in the desiccator, and is weighed when it is cold. The difference between the weight of the empty glasses and that of the glasses + filter gives the weight or *tare* of the filter.

The precipitate is next transferred to the filter and is washed and dried in the funnel as has been already described (53–60). It is finally allowed to cool in the glasses, and is weighed thus inclosed.

In order to make sure that the filter and its contents are perfectly dry, the cover-glass is removed and the drying process in the oven is repeated for twenty minutes. The filter is then covered, transferred to the desiccator, allowed to cool, and weighed again. These operations are repeated until two consecutive weighings do not differ by more than 1 milligram. From two to three hours usually suffice for drying a filter and precipitate in this way.

The weight of the precipitate + filter-paper is then readily obtained by subtracting the weight of the empty glasses from the last weighing; and from this the weight of the precipitate is obtained by subtracting the tare of the filter.

Usually the weight of the precipitate is obtained, by subtracting the weight of the glasses + filter, from the weight of the glasses + precipitate + filter. It is, however, advantageous to know the weight of the filter itself, in case the glasses should be broken before the final weighing has been taken.

Another Method is to adjust two similar filter-papers to precisely the same weight, by trimming the heavier one with scissors: one is then placed beneath the other in the funnel during filtration, washing and

drying, and the lower one is put, during the weighing, upon the pan with the weights as a counterpoise to the filter which contains the precipitate.

62. When the Precipitate requires to be Dried at a Temperature above 110° C., and to be Weighed without further Treatment, the weight of the filter dried at 100° is first determined; the weight of the filter and precipitate, after being dried at 100° C., is then ascertained (**61**).

Then a portion of the precipitate is removed from the filter to the watch-glasses (fig. 8, p. 12) and is weighed. This portion is then heated to the required temperature for at least twenty minutes, then cooled in the desiccator and weighed: and this process is repeated until the precipitate ceases to lose in weight. From the result thus obtained, the weight which the whole precipitate would possess, after having been dried at the higher temperature, can be calculated.

Ignition of Precipitates.

63. After the precipitate has been dried in the funnel, it is usually ignited before being weighed. In this process the filter is burnt and converted into ash; and the weight of this ash, which is usually less than 1 milligram, is subtracted from the total weight of the ignited precipitate and filter-ash.

It is accordingly necessary to determine the average weight of the ash of a filter-paper. Two sizes of filter-paper are usually employed. They are $3\frac{1}{2}$ and $4\frac{1}{2}$ inches in diameter respectively: the weight of the ash must be determined for each size.

64. The Weight of the Filter-ash may be determined as follows: — Six of the cut filter-papers are selected from different parts of the packet, or six circular filter-papers are cut of precisely the same size from different sheets of the paper. These are carefully folded and burnt, one by one, to

a perfectly white ash in a weighed platinum crucible. The crucible containing the ash is then weighed. The total weight of the ash thus obtained, when divided by six, will give the average weight of the ash from one filter-paper.

65. The Vessels used for the Ignition of precipitates are usually crucibles made of platinum, silver, nickel, or porcelain (figs. 49, 50). Occasionally a capsule or a dish is employed (figs. 47, 48).

Whenever it is admissible, a platinum crucible should be used. It can be more rapidly and more uniformly heated than a porcelain crucible, it resists the action of a coal-gas flame better than nickel does, and it is practically infusible. A crucible 1·25 inches in height and 1·25 inches in diameter will be found convenient for most purposes.

A small open platinum dish or capsule, will often be found convenient for the ignition of substances in place of a platinum crucible. It is about 2 inches in its greatest diameter, and has an extreme depth of about three-quarters of an inch.

The clean, empty crucible or capsule should always be heated to redness, and then be allowed to cool in the desiccator and weighed, before it is used.

66. A Platinum or Nickel Crucible or Capsule may readily be Cleaned by rubbing the metal with the moistened finger, which has been dipped into sea-sand. The sand should be examined through a lens. If the grains are seen to be rounded and pebble-like, the sand is suitable; but if they are angular the sand should be rejected, since it would scratch the metal.

If the stains are not removed when they are rubbed with sand, a little $KHSO_4$ may be fused in the vessel. The sulphate, when cold, is removed by boiling it with water, and the surface of the platinum is finally polished with sea-sand.

67. Prevention of Reduction or Oxidation during Ignition.— When a precipitate is being heated which can suffer reduction or deoxidation, care must be taken that the flame does not come into contact with the interior of the crucible, else reduction of the substance may take place. This is best avoided by applying a small flame to the bottom of the crucible, and slanting the crucible (fig. 50, p. 63).

When, on the other hand, oxidation during the ignition of the precipitate must be avoided, air is excluded by passing a current of gas. Rose's perforated lid and flanged porcelain tube (fig. 44) may be used

Fig. 44.

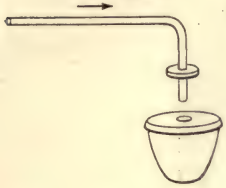


Fig. 45.

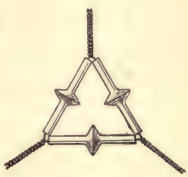
for this purpose. A slow stream of gas is conveyed into the crucible by the tube, and escapes from beneath the lid of the crucible.

An inverted clay tobacco-pipe, of suitable size, may replace Rose's lid and tube: the stem of the pipe serves as the tube, and the inverted bowl takes the place of the lid, as is seen in fig. 45.

68. The Crucible is usually Supported upon a pipe-clay triangle (figs. 48, 49, 50), or upon a triangle made of stout platinum wires twisted together (fig. 47).

The pipe-clay triangle may have a projecting edge in the middle of each side (fig. 46). This enables the flame to pass between the crucible and the triangle, and secures a more uniform heating of the crucible; it also strengthens the weakest parts of the triangle.

Fig. 46.



The triangle is usually supported over the flame by a tripod-stand (fig. 48, p. 62), or by the ring of a retort-stand (fig. 50, p. 63). Occasionally the burner itself serves to support the triangle (figs. 47, 48).

69. The Temperature and Duration of the Ignition of the precipitate will vary with its nature.

In all cases the heat should be applied gradually. This is especially necessary when the substance is imperfectly powdered, when it is not perfectly dry, or when it is in the form of a very light powder.

70. A convenient method of Igniting Precipitates at a comparatively Low Temperature is shown in figs. 47, 48. The crucible is placed upon a triangle which rests upon the chimney of a Wallace-Argand burner, the gauze

Fig. 47.

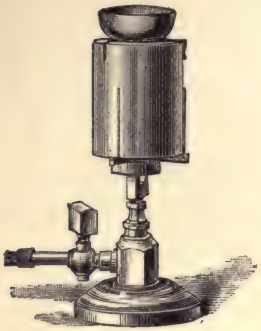


Fig. 48.

top of which has been removed. When the gas, issuing from the ring at the bottom of the burner, is kindled and is checked sufficiently by the tap, a current of heated air plays against the sides of the crucible; the crucible thus becomes uniformly heated without being soiled by contact with the flame. Any temperature up to a red-heat may be thus imparted to the crucible or capsule.

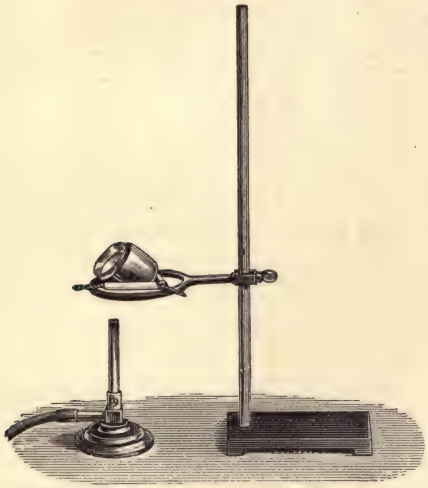
Fig. 49.

71. The Ordinary Method of Ignition at any temperature by means of a Bunsen-burner is shown in fig. 49. The crucible rests upon a pipe-clay triangle on the ring of a tripod-stand or of a retort-stand. A retort-stand (fig. 50) is generally to be preferred

as a support, since it enables the height of the crucible above the flame to be suitably adjusted, so as to expose the crucible to the desired temperature.

72. When Loss by Spirting might occur, the Substance is heated From Above.—The crucible containing the substance is then inclined as is shown in fig. 50. A

FIG. 50.



small flame is placed under the edge of the crucible, and the substance is heated partly by heat radiated from the lid, and partly by the conduction of heat down the side of the crucible.

This process is especially suitable when a liquid is being evaporated in the crucible.

IGNITION OF THE PRECIPITATE AND INCINERATION OF THE FILTER IN ONE PROCESS.

73. This method is employed when the combustion of the filter-paper can exert no reducing action upon the precipitate. It is carried out as is described below.

The filter and precipitate are first thoroughly dried in the steam-oven. The filter-paper, still containing the precipitate, is then folded together; and the free edge of the paper is turned down, so as to inclose the precipitate in as small a space as possible. The filter is then placed in the crucible, which is nearly covered with the lid, a small space only being left for the escape of the gases which are formed by the combustion of the filter-paper.

The heat must be applied with moderation at first. But as soon as the flame due to the burning of the combustible gases is no longer seen, the lid may be removed, and the heat may be increased until the required temperature is attained. After the filter-paper has been completely converted into ash, and the black carbon of the paper has been burnt, the source of heat is removed. As soon as the crucible has cooled below redness, it is removed by means of a pair of *clean* crucible-tongs to the desiccator. The crucible lid is then ignited until it is clean, and is placed upon the crucible. The crucible with its contents is weighed as soon as it is cold. It will usually require about twenty minutes for cooling.

If the Filter-paper is Difficult to Incinerate, and black particles of carbon persistently remain, the combustion may be hastened by bringing the portions of unburnt filter-paper against the hottest portion of the crucible by means of a stout platinum wire, which has been fused into a piece of glass tubing to serve as a handle. A small blowpipe flame may be used to produce a higher temperature, and thus aid in effecting the complete incineration of the paper. Another plan for hastening the combustion of the carbon is to introduce a gentle stream of oxygen into the crucible. Or the cold ash may be moistened with a drop of saturated ammonium nitrate solution, and then be carefully dried and again ignited.

Ignition of the Undried Precipitate.—Some precipitates, such as $Al_2(HO)_6$ and $Cr_2(HO)_6$, which have been washed and drained by means of the filter-pump, may be ignited without having been previously dried in the steam-oven. In this case the lid must cover the crucible until all the moisture and gases have been expelled, and the heat must be very gradually applied, starting with a small flame placed at some distance below the crucible.

EXPERIMENT 16.—Carefully wrap up the precipitate of $Al_2(HO)_6$, which has been already dried (60), and place it in a platinum or

porcelain crucible, which has been recently ignited and weighed. Nearly cover the crucible with the lid. Ignite the crucible, placed in an upright position (fig. 49, p. 62), very slowly at first. Then gradually increase the temperature until the crucible becomes red-hot. Maintain this temperature for ten minutes, and finally heat the crucible over the table-blowpipe flame to bright redness for five minutes.

Allow the crucible to cool somewhat; then transfer it to the desiccator by means of the crucible-tongs; and weigh it as soon as it is cold. Heat the crucible once more by the blowpipe-flame, cool it in the desiccator, and weigh it again. Repeat this process, if necessary, until the weight does not become reduced by more than 1 milligram, by the last ignition.

From the original weight of the salt used (**52**, Exp. 11), and the weight of the precipitate (Al_2O_3) obtained after ignition, the percentage of aluminium in potassium alum may be calculated.

The method of entering the results of the weighings and of making the calculations is shown below.

Estimation of Al in $AlK(SO_4)_2.12H_2O$:—

First weight of bottle + alum, ...	19·8635
Second weight of ditto, ...	18·3980
Weight of alum used, . . .	1·4655
Weight of precipitate (Al_2O_3) + crucible + filter-ash, .	16·7403
Weight of crucible alone, ...	16·5809
	0·1594
Weight of filter-ash, . . .	0·0022
Weight of Al_2O_3, ...	0·1572

The weight of aluminium in this Al_2O_3 is found by the following proportion :—

As molecular weight of Al_2O_3 : molecular weight of Al_2 : : weight of Al_2O_3 found : weight of Al.

Or, as 102·16 : 54·16 : : 0·1572 : : 0·08334

And the percentage of aluminium in the salt is found by the proportion :—

As weight of substance taken : weight of Al found : : 100 : percentage weight of Al.

Or, as 1·4655 : 0·08334 : 100 : : 5·69

The two proportion statements above may be combined into one compound proportion statement as follows :—

102·16 : 54·16 : : 0·1572 : weight of Al

1·4655 : weight of Al : 100 : : percentage of Al

Hence the percentage of $Al = \frac{54{\cdot}16 \times 0{\cdot}1572 \times 100}{102{\cdot}16 \times 1{\cdot}4655} = 5{\cdot}69$

Now the percentage of Al actually present in potash alum is found by the proportion

Molecular weight of alum.			Weight of Al.
474·41	:	100 : :	27·08 : 5·59

Hence the error of the estimation = 5·69 − 5·59 = + 0·10

Ignition of the Precipitate, and Separate Incineration of the Filter.

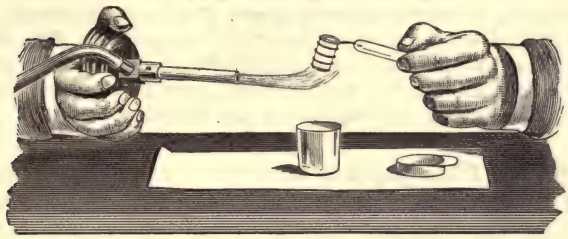
This process is employed when the combustion of the filter-paper might exert a reducing action upon the precipitate, and in cases in which it is desirable to keep the precipitate apart from the ash. Three methods of carrying out this process are described below.

74. The Filter is Burnt in a Platinum-wire Coil, and the Ash and the Precipitate are Ignited together in the Crucible. The dry precipitate and filter are taken from the funnel, and the precipitate is carefully shaken out of the filter into the crucible or capsule.

The crucible should meanwhile be placed on a piece of glazed paper (fig. 51), which serves to catch any particles of precipitate which may fall outside the crucible. For dark precipitates white paper may be used, but for light-coloured precipitates dark paper is preferable. Any particles of the precipitate which remain adhering to the filter-paper should be detached as far as possible by gently rubbing the sides of the filter-paper together, and should then be transferred to the crucible.

The filter-paper is then folded up as is shown in fig. 52, and is finally rolled up as is shown in fig. 53, and bound by a piece of platinum wire, which is coiled round it in a spiral

FIG. 51.

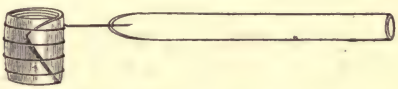


form. A piece of fairly stout platinum wire about 6 inches in length, one end of which has been fused into a piece of glass-tubing to serve as a handle, will be found suitable.

The filter-paper is then kindled by a Bunsen-flame, and is kept glowing, by occasionally introducing it into the flame, until the carbon is burnt away. A slight tap of the wire on

FIG. 52.

FIG. 53.



the edge of the crucible will cause the ash to fall into the crucible. If the wire has been coiled into a *conical* spiral, the folded filter may be dropped into it, and the ash may be readily turned out after the ignition by simply inverting the spiral.

Any particles of the precipitate or of the filter-ash which may have fallen upon the sheet of paper are then carefully transferred to the crucible by means of a small camel's-hair brush, and the crucible and its contents are ignited, allowed to cool in the desiccator, and weighed.

75. If the Precipitate contains a Metal, which may be Reduced by the Filter during its Incineration, and may then alloy with the platinum wire, great care must be taken to fold the filter so as to

inclose the adhering precipitate in the *middle* of the paper coil. Or the wire may be dispensed with, and one of the methods of incineration which are described in pars. **77**, **78** may be employed.

76. If the Substance is Altered in Composition by Contact with the Burning Filter, it is usually necessary to treat the filter-ash with some liquid, in order to restore that part of the substance which has been ignited on the paper to its original composition. The ash is then allowed to fall upon a separate part of the bottom of the crucible or capsule. The ash can then be treated apart from the precipitate. Alternative methods are described in pars. **77** and **78**.

77. The Filter-paper is Incinerated on the Crucible lid, and the Precipitate is Ignited in the Crucible, and both are ultimately weighed together. The precipitate is shaken out into the crucible, and the last traces are detached from the paper as completely as possible.

The filter-paper is then cut up into strips by a clean pair of scissors, and these strips are incinerated one by one upon the inverted lid of the crucible, which is supported on a pipe-clay triangle. The crucible and lid are then ignited together. The filter-paper may be incinerated in a separate crucible instead of on the lid.

78. The Filter is Burnt in the Crucible, and the Precipitate is then Added and Ignited. This method gives satisfactory results with careful manipulation: but it will be seen that a greater risk of loss of precipitate is incurred than by the preceding methods. The procedure is as follows.

The precipitate is carefully transferred to a clock-glass or to a piece of glazed paper, and is then covered with an inverted funnel (fig. 54). The filter-paper is then folded up and is incinerated by heating it in the crucible.

Or the filter may be held over the crucible by the crucible-tongs in the Bunsen-flame, until most of the carbon is burnt off; the residue is allowed to drop into the crucible, and the incineration is finished in the crucible over the Bunsen-flame.

The precipitate is then placed in the crucible, a *small*

camel's-hair brush, or smooth spatula, being used to sweep off the last particles from the glazed surface. Finally, the crucible and its contents are ignited at the required temperature.

EXPERIMENT 17.—The precipitate of $BaSO_4$, which has been obtained from alum, and has been washed and dried (**60**), is ignited according to the first method (**74**).

The precipitate is detached as far as possible from the filter-paper, and is allowed to fall into a platinum crucible standing upon black glazed paper.

The filter-paper, which still retains some of the precipitate, is carefully folded and bound round by a platinum wire spiral. It is then held over the crucible, and is kindled by a Bunsen-flame applied to it

FIG. 54.

in the manner shown in fig. 51. When the paper has been burnt to a white ash, this ash is shaken into the crucible by gently tapping the wire against the edge of the crucible.

Since the burning of the filter-paper may have reduced the adherent $BaSO_4$ to BaS, it is necessary to insure the reconversion of this into $BaSO_4$ in the following way. The ash is moistened with one or two drops of dilute HCl, and then with one drop of dilute H_2SO_4. The lid is then placed on the crucible, and the crucible is heated *very* gently over the Bunsen-flame. As soon as all the liquid has been evaporated, the crucible is gradually raised to a dull red heat, and is kept at that temperature for about fifteen minutes. The crucible is then allowed to cool in the desiccator, and is weighed. It is again heated for ten minutes at the same temperature, and is weighed again as soon as it is cold. These operations are repeated as long as the crucible loses weight.

From the weight finally obtained, the weight of the $BaSO_4$ can be found: and from this the percentage weight of SO_4 in the alum used can be calculated.

The following example will serve to illustrate the methods of entry and of calculation :—

Estimation of SO_4 in $AlK(SO_4)_2 12H_2O$:—

First weight of bottle + salt, . . .	15·8723
Second weight of bottle, ...	14·7954
Weight of salt used, . . .	1·0769
Weight of crucible + $BaSO_4$ + ash, . . .	17·6415
Weight of crucible alone, ...	16·5806
	1·0609
Weight of filter-ash, . . .	0·0022
Weight of $BaSO_4$, . . .	1·0587

The weight of SO_4 in the $BaSO_4$ is then found by the following proportion :—

$BaSO_4$ SO_4 $BaSO_4$ found
233·06 : 96·06 : : 1·0587 : 0·4363 gram SO_4

And the percentage weight of SO_4 in the potassium alum is then calculated from the weight of the alum used, by the following statement :—

1·0769 : 0·4363 : : 100 : 40·52 SO_4 per cent. (Found).

Now the percentage weight of SO_4 actually present in alum is calculated from the above formula for alum by the following statement :—

Alum $2SO_4$
474·41 : 192·12 : : 100 : 40·50 SO_4 per cent. (By Theory).

Hence the error in the estimation = 40·52 − 40·50 = + 0·02.

Preparation of Pure Substances by Crystallisation.

The Use of Pure Substances, both for practice in analytical processes and as reagents, is generally indispensable in quantitative analysis. Pure chemicals can now usually be purchased, but some general methods of purifying substances are given here, in case the analyst may require to use them. Fuller details will be found in Section VII. of *Clowes' Practical Chemistry*.

79. The Process of Crystallisation is applied to the preparation of two classes of pure substances.

Firstly. The purity of a soluble and crystallisable chemical compound can usually be insured by repeated crystallisation from solution in a suitable medium, since by this treatment the impurities which were present in the original substance are left behind in the mother-liquor. Many commercial salts may be completely purified by crystallising them once or twice from their solution in water (**80**).

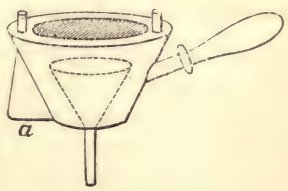
Secondly. Double salts can usually be made by dissolving their component salts in suitable proportions in as little hot water as possible, and crystallising the solution. It should be noted, however, that in the preparation of a double salt, it is frequently necessary to mix the component salts in proportions different from those in which they are present in the double salt (**81**).

80. In the Crystallisation of Salts or of Simple Bodies, the following is the usual mode of procedure.

A beaker, or flask, or a porcelain dish is used for the solution of the solid. A hot and nearly saturated solution of the solid is made in water or in some other suitable liquid, by stirring the coarsely-crushed solid with the hot liquid until the solid no longer dissolves. The hot solution is then decanted from the excess of solid into a crystallising dish.

If any suspended matter is present, the solution must be passed through a filter, in a funnel which is surrounded by hot water. The apparatus which is used for this purpose is shown in fig. 55. It consists of a double-walled copper vessel in the shape of a truncated cone. In communication with the interspace of this, is a hollow projection (*a*). The apparatus is half-filled with water. The water is then heated to boiling by placing a Bunsen-flame beneath the projection (*a*), which

FIG. 55.



is filled with water communicating with that in the jacket. In this way hot water will circulate throughout the copper jacket, and thus the funnel which is supported in it may be kept hot during filtration.

The clear hot solution is now surrounded with a vessel containing cold water, so as to cool down the solution rapidly and induce the formation of small crystals. As soon as the crystals have ceased to form, the supernatant liquid is poured off, and the crystals are placed upon a porous tile to drain. After the crystals have drained for several hours, they are broken up, and are finally dried by pressing them between folds of filter-paper. They are then preserved in a well-stoppered bottle.

EXPERIMENT 20.—Weigh out roughly 250 grams of potassium alum, $AlK(SO_4)_2.12H_2O$, and dissolve it in 200 c.c. of boiling distilled water. Filter the solution, if necessary ; cause it to crystallise by cooling it ; and then dry the crystals as is described above, and place them in a clean, dry, stoppered bottle.

EXPERIMENT 21.—Weigh out roughly 250 grams of copper sulphate crystals, $CuSO_4.5H_2O$; dissolve the salt in 250 c.c. of boiling distilled water, crystallise, dry the crystals, and place them in a bottle for subsequent use.

Some of the following salts may also be crystallised for practice. They will be of use in estimations, which are described in later parts of this book :—

KCl ; AmCl ; $MgSO_4.7H_2O$; $BaCl_2.2H_2O$; $ZnSO_4.7H_2O$; $Pb(C_2H_3O_2)_2.3H_2O$; $K_2Cr_2O_7$; and $H_2C_2O_4.2H_2O$.

81. In the Formation and Crystallisation of Double Salts, the mode of procedure varies with the properties of the substances to be used.

(a). The usual method of preparing a double salt consists in weighing the simple salts in the proportions in which they are contained in the double salt. A hot strong solution is then made of each salt separately ; these two solutions are mixed together, and the liquid thus obtained is crystallised (80).

(b). This method, however, cannot always be employed,

since when certain double salts are dissolved in hot water, they suffer partial decomposition into the original salts. Hence a solution of their component salts, prepared as is directed above, will furnish on crystallisation not only crystals of the double salt, but also of one of the component salts. This difficulty is met in the following preparation by using an excess of $MgSO_4.7H_2O$.

EXPERIMENT 22.—**Preparation of $MgSO_4.K_2SO_4.6H_2O$.** Weigh out 174 grams of pure K_2SO_4 and 320 grams of pure $MgSO_4.7H_2O$. It will be noticed that the weight of the $MgSO_4.7H_2O$ is in excess of the molecular proportion for the reason already stated. Dissolve these portions separately in boiling distilled water; mix the solutions. crystallise, and dry the crystals of the double salt.

(c). In the preparation of double salts, it must also be remembered that certain salts, when they are treated with hot water, are converted partially into insoluble basic salts. Hence boiling water must not be employed in dissolving them. The following preparation will serve as an example.

EXPERIMENT 23.—**Preparation of $Fe(NH_4)_2(SO_4)_2.6H_2O$.** Weigh out 132 grams of pure Am_2SO_4, and 278 grams of pure recrystallised $FeSO_4.7H_2O$. It will be noticed that these weights are in molecular proportion. Dissolve each of these salts separately in the smallest possible quantity of distilled water, at a temperature not exceeding 40° C. : then mix the two solutions, add a few drops of dilute sulphuric acid, cool, crystallise, and dry the crystals (**80**).

(d). Some double salts are most readily and completely separated from solution by pouring the solution into a liquid in which the salt is insoluble. Thus the solution of ferrous-ammonium-sulphate (Exp. 23) may be poured into alcohol, when the double salt at once separates in a granular condition. The yield of the salt which is furnished by this method is also larger than that obtained by crystallisation.

The following Double Salts may also be Prepared, using the molecular proportions of the component salts denoted by the formulæ of the double salts. The weighed salts are dissolved in the least possible quantity of boiling water, and are treated as has been described above.

$Al_2(SO_4)_3.K_2SO_4.24H_2O$; $Cu(NH_4)_2(SO_4)_2.6H_2O$; $CuCl_2.2AmCl.2H_2O$.

Other Ways of Preparing Pure Substances.

82. By Precipitation (52) and subsequent Washing (53) and Drying (59) many chemicals may be prepared in a pure state.

Experiment 24.—**Preparation of Pure $CaCO_3$.** Dissolve 100 grams of pure calcium chloride in 250 c.c. of distilled water. Heat the solution to boiling, filter if necessary, and then add a strong solution of pure Am_2CO_3 as long as any precipitate is caused. Allow the precipitate to subside, and wash it by decantation. Then transfer the precipitate to a filter and wash it with hot water until the washing-water no longer gives any turbidity with $AgNO_3$, showing that all the dissolved chloride has been washed away.

Finally, dry the precipitate in the steam-oven, detach it from the filter-paper, and place it in a bottle for further use.

Pure $BaCO_3$ and $SrCO_3$ may be prepared in a similar way.

Experiment 25.—**Preparation of Pure NaCl.** Dissolve 100 grams of NaCl in 400 c.c. of distilled water. Precipitate the NaCl by passing into this solution a current of HCl gas, which has been washed by passing through a bottle containing a little water. The delivery tube should have attached to it, by means of a piece of india-rubber tubing, an inverted funnel, the mouth of which dips just beneath the surface of the sodium chloride solution. This precaution is necessary to prevent the salt solution from ascending the delivery tube.

As the gas passes into the solution, the NaCl will be precipitated in small crystals. As soon as the precipitation ceases, the NaCl is washed twice by decantation (53) with pure strong HCl. The salt is then placed upon a porous tile to drain, and is finally freed from HCl and from water, by heating it in a porcelain dish over a small Bunsen-flame.

This pure dry NaCl is preserved for use in a bottle.

Experiment 26.—**Preparation of Pure Anhydrous Tartar Emetic ($KHC_4H_3(SbO)O_6$).** Dissolve 100 grams of tartar emetic in the smallest possible quantity of water. Add to this solution about twice its volume of methylated spirit. Wash the salt, thus precipitated, with methylated spirit, and dry it at once in the steam-oven.

83. Sublimation is occasionally used for the purpose of separating volatile from non-volatile substances, and thus effecting their purification. If a volatile substance is to be

purified, sublimation may be effected by placing the substance in a porcelain crucible, and inverting over it a similar vessel. The lower crucible is then gently heated; the substance will volatilise and condense in the upper crucible, which must be replaced if it becomes hot.

Another method consists in heating the substance in a porcelain dish, and condensing the vapour by means of an inverted funnel placed as a cover to the dish.

Unless the substance which is to be sublimed is known to be perfectly dry, it is best to allow the first portion of its vapour to escape and carry off the moisture with it.

EXPERIMENT 27.—**Purification of Iodine.** Partly fill a porcelain crucible with a finely-powdered and intimate mixture of three parts of iodine with one part of potassium iodide. Cover this with a second crucible, and heat the mixture gently. Remove the sublimed crystals from the upper crucible, and store them in a clean dry bottle.

The mixture of the iodine with potassium iodide serves to free it from bromine and chlorine:—$Cl + KI = KCl + I$.

EXPERIMENT 28.—**Resublimation of As_2O_3.** Introduce into a small porcelain dish a thin layer of As_2O_3. Invert over this a clean glass funnel, and heat the dish gently. Detach the sublimed As_2O_3 from the funnel, and keep it in a bottle for future use.

GENERAL RULES TO BE OBSERVED WHILST WORKING.

84. It will have been noticed that many rules and precautions have already been given among the general directions for weighing, precipitation, and other processes performed in analysis. In the following statement many of these directions are summarised, and others are added which will be of great assistance to the student.

1. Before commencing work, see that the requisite reagent bottles are filled, and filter those liquid reagents which are not clear. Keep the bench surface scrupulously clean and dry during work.

2. All the apparatus required for use should be perfectly clean.

Glass and porcelain vessels may usually be cleansed by washing them with the brush. Strong acid or caustic alkali solution may be requisite. If these reagents fail, the surface may often be cleansed by rubbing it with moistened sea-sand, or by shaking water containing sea-sand round in the vessel.

Grease is generally removed by the application of hot solution of caustic alkali.

Metal crucibles and dishes are cleansed and polished by rubbing them with moist sea-sand, the round grains of which do not scratch the metal surface.

The stains on a platinum crucible are readily removed by fusing a little $KHSO_4$ inside the vessel, or by dipping it into the fused salt if the stains are on the outside.

3. Before commencing the quantitative analysis of a substance of unknown composition, a careful qualitative analysis should invariably be made.

4. Before starting any analytical process, which is unknown by previous experience, read carefully through *the whole* of the description of it, and master the details of the description.

5. Never place a substance directly on the scale-pan of the balance, but put it on a watch-glass or other suitable support.

6. No body which gives off corrosive gas or vapour should be weighed on a delicate balance, unless it is contained in an accurately-stoppered vessel.

7. When a weighing is finished, note down the weight at once in the Note-book and check it. Take care that the weight is entered correctly, as one wrong weighing will spoil an analysis.

8. Never leave weights on the scale-pan after a weighing is finished and recorded.

Always close the balance-case as soon as a weighing is finished.

9. All bodies, after they have been heated, should be allowed to cool in the desiccator before they are weighed: they should be weighed as soon as they are cold. *Never* allow a substance to remain very long in the desiccator before weighing it.

Crucibles should be heated shortly before they are used, then allowed to cool in the desiccator and weighed. These processes should be repeated each time a crucible is used.

10. Platinum vessels and other metallic vessels which have been heated to redness, should never be touched with brass crucible-tongs until they have cooled below redness.

11. Avoid splashing in filtering and pouring off liquids. Always pour liquids from one vessel to another by means of a wetted glass rod, pressing the rod against the edge of the upper vessel, and thus conducting the liquid to the side of the lower one. If the outer edge of the upper vessel is greased where the liquid is poured, the liquid will be prevented from running down the outside of the vessel.

12. Vessels of porcelain, nickel, or platinum should be used in preference to glass vessels for holding alkaline liquids. Nickel and silver basins and crucibles should not be used with acid liquids. Platinum should not be used in the presence of aqua regia, of nitric acid and a chloride, of hydrochloric acid and a nitrate, or of caustic alkalis.

13. Platinum vessels should not be used for heating reducible compounds of As, Sb, Zn, Pb, Sn: nor should they be used for alkalis, or for alkaline nitrates or cyanides, or for reducible or fusible phosphates. Free carbon and silicon are also very injurious to platinum at high temperatures.

A platinum vessel is rendered brittle by being heated for any length of time in a gas-flame which deposits carbon.

14. Vessels which require to be heated to high temperatures should be supported on platinum, pipe-clay or fire-clay supports. Porcelain and other dishes, when they are heated on a water-bath and require subsequent weighing, should be supported on glass rings.

15. A flame which is used for heating crucibles should be free from luminosity and strong colour. If the flame is luminous it will deposit soot on the vessels with which it is in contact. If it is coloured, it will probably deposit zinc or copper, or their oxides, upon the vessel upon which it plays.

16. When work ceases, and an operation is unfinished, the vessels containing the substances should be labelled before being put away. *Never trust to memory in these matters.*

Calculation and Entry of Results of Analysis.

85. Entry in the Note-Book.—A Note-book of not less than quarto size will be found convenient for the entry of results obtained by quantitative analysis. The description and general results of the analytical process may be entered on the right-hand page, the left-hand page being reserved for the necessary calculations.

Each stage of the analysis should be carefully and accurately entered in the Note-book as soon as it is completed.

The rough entry in the laboratory may conveniently be made in pencil. Pencil writing is not obliterated by the chemical action of acids or of alkalis, as is the case with writing made by various kinds of ink.

When quantitative analysis is done under a teacher's direction, the student may advantageously copy out in ink, in a second Note-book, all the examples worked by him; and no estimation should be considered as completed until its

entry has been carefully examined, checked, and initialled by the teacher.

A difference of 0·2 per cent. from the theoretical quantity, or from the result of a duplicate analysis, is the maximum error which is usually allowed in the case of simple quantitative estimations.

86. Example of Entry in the Note-Book.—The following will serve as an example of the method of full descriptive entry recommended for the student's Note-book :—

Estimation of the amount of Water in $CuSO_4.5H_2O$.—1·8645 grams of the coarsely-powdered recrystallised salt were carefully weighed in the watch-glasses and clip. The air-oven was next regulated so as to maintain a uniform temperature of 210° C. The watch-glass containing the salt was placed upon a pipe-clay triangle in the air-oven.

The salt was heated in the oven for two hours. The glass containing the copper sulphate was then taken out, the upper glass and clip were quickly replaced, and the glasses were allowed to cool in the desiccator, and were weighed. The salt was again placed in the air-oven and heated for half an hour. It was then allowed to cool, and was weighed again. These processes were repeated until no further loss of weight occurred.

Weight of glasses and salt, ...		24·7840
Weight of glass alone, ...		22·9195
Weight of salt taken, ...		1·8645
Weight of glasses and salt, ...		24·7840
,, after 2 hours' drying,	24·1125	24·1115
,, after another half-hour,	24·1115	
Weight of water driven off, . . .		0·6725

Hence 1·8645 grams of the salt contain 0·6725 grams of water.

$$\therefore \text{ Percentage weight of water} = \frac{0{\cdot}6725 \times 100}{1{\cdot}8645} = 36{\cdot}06.$$

The calculated percentage of water,	= 36·13
The percentage found, . . .	= 36·06
Error, ...	= −0·07

87. Calculation of Results of Analysis.—Several examples have been given of the method of calculating the percentage of a substance present from the weight actually obtained. These calculations may be shortened in most cases by the use of "factors," and by the use of logarithms.

88. The Use of Factors.—The process of calculation may be shortened by multiplying the result obtained by the analysis by a factor. A table of such factors will be found in the Appendix. The following example applied to the calculation on page 65, will illustrate this.

In this estimation 0·1572 gram of Al_2O_3 was found. The factor to be used here to convert Al_2O_3 into $Al_2 = \frac{Al_2}{Al_2O_3} = \frac{54{\cdot}16}{102{\cdot}16} = 0{\cdot}53015$. Hence the weight of Al found $= 0{\cdot}1572 \times 0{\cdot}53015 = 0{\cdot}08334$. From this number the percentage may be calculated as before.

89. The Use of Logarithms.—The process of calculation may also usually be shortened by the use of logarithms. The logarithms used should consist of at least five figures. Logarithms corresponding to the factors mentioned above (88) will be found in the Appendix.

PART II.

SIMPLE GRAVIMETRIC ESTIMATIONS.

Introductory Remarks.—In the following descriptions of the processes for estimating various substances the most important and typical processes are printed in ordinary type. Those which are of less importance are printed in smaller type, and are placed, as far as is possible, after the typical estimation which they most nearly resemble. The estimations of metals and acid-radicles are generally arranged as exercises of increasing difficulty, rather than in the order of their analytical groups. For additional methods of estimation the student may consult *Fresenius' Quantitative Analysis.*

In most of the exercises the substance upon which the process of estimation is carried out is of known and definite composition. The accuracy of the student's result can therefore be checked by calculating from the formula of the substance the percentage of the constituent present. When the body is of unknown composition, it is best to make two estimations. It is usual to consider the percentage results sufficiently accurate if they do not differ by more than 0·2 from one another or from the theoretical result. The ordinary methods of calculation and of stating results will be found in the Examples in paragraphs 73, 78, 86, and 86–89.

It will be noticed that the substances which are usually given for practice are soluble in water. If a substance in which an estimation has to be made is insoluble in water, the student should ascertain, by experiments made upon a small portion of the finely-powdered body, what is the most suitable means of obtaining it in the dissolved state. The

acids may be tried as solvents in the following order:—hydrochloric acid, nitric acid, then a mixture of these two acids.

If treatment with these solvents does not effect solution, the substance may generally be decomposed by fusing it with about six times its weight of a mixture of sodium and potassium carbonates. The fused mass, after cooling, is then fully extracted with water, and the well-washed insoluble residue is dissolved by treatment with acid.

The process of treatment of an insoluble substance will probably be familiar to the student from his qualitative work. The special precautions necessary when using this process in quantitative analysis will be understood by reference to paragraphs **97** and **99**.

Estimation of Copper in its Soluble Compounds.

90. The Copper is precipitated as Hydroxide by solution of Potassium or Sodium Hydrate; the precipitate is ignited, and is weighed as CuO.

Note.—It is important to bear in mind that copper cannot be completely precipitated from its solutions by alkaline hydrate, in the presence of a large quantity of alkaline nitrate.

The presence of certain non-volatile organic substances also prevents the complete precipitation of copper from its solutions by potassium hydrate. Organic substances should therefore be completely destroyed before the copper is precipitated by potassium hydrate. This may be effected by adding sodium carbonate and potassium nitrate to the solution, evaporating to dryness, and fusing the residue. The copper is then dissolved out of the residue by heating it with dilute hydrochloric acid, and the filtered solution is treated as is directed below.

Copper may, however, be completely precipitated from its solutions in the form of sulphide, even in the presence of organic substances, or of an alkaline nitrate (**403**).

Weigh out accurately about 1 gram of crystallised copper sulphate, $CuSO_4.5H_2O$ (Exp. 21, **80**), into an 18-oz. beaker, or, better, into a porcelain or platinum dish (**84**, 12). Dissolve the salt in about 100 c.c. of distilled water, and if the liquid is not clear add a few drops of dilute HCl.

Cover the beaker or dish with a clock-glass to prevent loss by spirting, and heat the solution to boiling. As soon as the solution boils remove the flame, take off the clock-glass, and add boiling potassium hydrate solution gradually until it is in excess. Then boil the liquid again, and allow the precipitate to subside.

In order to ascertain whether KHO is present in excess, stir well, then allow the precipitate to subside, and observe whether the supernatant liquid has become colourless; also test the clear liquid with turmeric-paper. If the liquid is colourless, and gives a brown stain on the paper, the presence of excess of the alkali is indicated. The addition of a *large excess* of the alkali should be avoided.

The clear liquid is now decanted through a filter, using the filter-pump (56) to hasten the process. The precipitate is twice washed by decantation by boiling it with water (53); it is then transferred to the filter by means of a wash-bottle with a fine jet, and a glass rod tipped with rubber. The washing is continued until the washing-water ceases to give an alkaline reaction; it is then further proceeded with, until a few drops of wash-water from the funnel no longer give a white precipitate when they are warmed with $BaCl_2$ solution and allowed to stand for five minutes.

As soon as the precipitate has been completely washed, the precipitate and filter are dried in the funnel in the steam-oven (p. 33). The filter is then burnt apart from the precipitate (74–78) in the following manner.

The precipitate is detached from the filter as *completely as possible*, and is placed in a crucible, preferably of platinum. The filter is then folded up with the soiled surface in the middle, and is bound round with a spiral of platinum wire. It is then burnt in the Bunsen-flame till all the carbon is consumed. The crucible is then tapped upon the bench, so as to cause the precipitate to collect on one side, and the filter-ash is dropped by itself upon the other side of the bottom of the crucible.

The filter-ash is then moistened with two drops of strong HNO_3, and is gently heated until the excess of the acid has been driven off. The crucible and its contents are then heated to redness for fifteen minutes, and are weighed after they have cooled in the desiccator.

The ignition is repeated for another five minutes, and the cold crucible is again weighed: and these operations are repeated until the weight is constant.

The weight of CuO thus obtained from the known weight of the salt, enables the percentage of copper in the crystallised salt to be calculated.

Other Methods of Estimation for Copper will be found in pars. 335–338, 403.

Estimation of Nickel in its Soluble Compounds.

91. The Nickel is precipitated as Nickelous Hydroxide; this is converted into Oxide, NiO, by ignition, and is weighed as such.

Note.—If non-volatile organic substances are present, these must be removed before precipitating the nickel (90, *Note*).

Weigh out accurately about 1 gram of pure nickel ammonium sulphate, $Ni(NH_4)_2(SO_4)_2.6H_2O$ (81), into an 18-oz. beaker, or, better, into a porcelain or platinum dish. Dissolve the salt in about 100 c.c. of water, and add potassium hydrate solution in excess. Heat the liquid for some time nearly to boiling, allow the precipitate to settle, then wash it with hot water three or four times by decantation. Transfer the precipitate to a filter, and continue to wash it until the washings cease to give a precipitate with barium chloride solution.

Dry the precipitate in the steam-oven, and ignite it in a platinum crucible apart from the filter (77, 78). Heat the crucible at first in the Bunsen-flame, and finish by heating it strongly in the blowpipe-flame. Care must be taken that the flame does not enter the crucible, else the result will be low, owing to the reduction of the oxide of nickel to metallic nickel.

It is difficult to get rid of the last trace of alkaline hydrate and salt, even by long-continued washing of the precipitate. Hence it is necessary in very accurate determinations to extract the ignited precipitate with water, as is described in the estimation of Mn (129), and then to dry, ignite, and weigh the precipitate once more.

From the weight of NiO thus obtained, the percentage of nickel may be calculated.

Estimation of Iron in its Soluble Compounds.

92. The Iron is precipitated as Ferric Hydroxide; this is ignited and weighed as Ferric Oxide, Fe_2O_3.

Note.—If non-volatile organic substances are present, these must be removed before precipitating the iron (**90**, *Note*).

Weigh accurately about 1·5 grams of ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2.6H_2O$ (**81**), into an 18-oz. beaker, or, better, into a porcelain or platinum dish (**84**, 12). Dissolve this in about 100 c.c. of distilled water, containing a few drops of dilute sulphuric acid.

Heat the solution with sufficient strong nitric acid to convert the ferrous salt into the ferric condition. This change may be known to be nearly complete, as soon as the further addition of a drop of strong nitric acid causes no brown colour in the solution. The change to ferric salt should be proved to be complete, by adding a small drop of the dilute solution to a drop of freshly-prepared potassium ferricyanide solution on white porcelain, when no blue colour must appear.

While the liquid is still hot add AmHO solution in excess, and boil. The precipitate may be washed twice by decantation (**53**); it is then transferred to the filter, the filter-pump being used to hasten the filtration (**56**). The washing is continued, until the washing-water gives no precipitate with $BaCl_2$ solution.

The precipitate is dried in the steam-oven, and is then transferred to a crucible; the filter is incinerated apart (**74–78**) and is added to the precipitate, which is then ignited at a bright red heat over the Bunsen-flame until its weight is constant.

From the weight of the Fe_2O_3 thus obtained, the percentage of iron may be calculated.

Solutions of Ferric Salts will not require the above preliminary treatment with nitric acid, but may be precipitated at once with AmHO solution.

Volumetric Methods of Estimation for Iron will be found in pars. **258–261**, **268** and **269**.

Estimation of Aluminium in its Solutions.

93. The Aluminium is precipitated by Ammonium Hydrate solution, as Aluminium Hydroxide: this is converted into Oxide, Al_2O_3, by ignition, and is weighed as such.

Note 1.—If non-volatile organic substances are present, these must be removed before the Al is precipitated (**90**, *Note*).

Note 2.—If the student has already made this estimation in working through Part I., it need not be repeated here.

Weigh out accurately about 1·5 grams of pure recrystallised potassium alum, $AlK(SO_4)_2.12H_2O$ (Exp. 20, **80**), into an 18-oz. beaker, or, better, into a porcelain or platinum dish (**84**, 12). Dissolve the salt in about 100 c.c. of water, add ammonium chloride solution in moderate quantity, and then add ammonium hydrate solution in *slight* excess. Cover the dish with a clock-glass, and heat to boiling. Continue boiling until the liquid smells only faintly of ammonia.

Wash the precipitate by decantation, and transfer it to a filter, using the filter-pump to facilitate filtration (**56**). Continue to wash the precipitate upon the filter until the washing-water is free from sulphate; dry the filter and precipitate in the steam-oven; and ignite the precipitate together with the filter in a platinum crucible (**73**, Exp. 16). Heat the crucible gently at first, and finally expose it to a white heat over the blowpipe-flame. Repeat the ignition until the weight becomes constant.

From the weight of Al_2O_3 thus obtained, the percentage of aluminium may be calculated.

Estimation of Chromium in Solutions of its Compounds.

94. The Chromium is precipitated by Ammonium Hydrate as Hydroxide: this is converted into Oxide, Cr_2O_3, by ignition, and is weighed as such.

Note.—If non-volatile organic substances are present, they must be removed before precipitating the chromium (**90**, *Note*).

Weigh out accurately about 1 gram of pure recrystallised chrome-alum, $CrK(SO_4)_2.12H_2O$, into a porcelain or platinum dish. Dissolve the substance in about 100 c.c. of water, and add a slight excess of ammonium hydrate solution. Then heat the contents of the dish to a temperature just below the boiling-point, and continue the heating until the supernatant liquid becomes perfectly colourless.

The precipitate is then filtered, washed, dried, and ignited in the same manner as was described in the estimation of aluminium (**93**).

From the weight of the Cr_2O_3 thus obtained, the percentage of chromium is calculated.

Estimation of Chromium in a Soluble Chromate.

95. The Chromate is reduced to a Chromium Salt by Sulphurous Acid, or by some other suitable Reducing Agent: the Chromium is then precipitated as Hydroxide, and is estimated as is described above (94).

Weigh out accurately about 1 gram of pure potassium dichromate, $K_2Cr_2O_7$, and dissolve it in about 100 c.c. of water. Add a strong aqueous solution of sulphur dioxide, or pass sulphur dioxide gas through the liquid, until the red colour of the solution changes to pure bluish-green.

Estimate the chromium in this solution in the same manner as has been described above (**94**).

A Volumetric Process of Estimation for Chromate will be found in par. 297.

Estimation of (SO_4) in a Soluble Sulphate.

96. The (SO_4) is precipitated as $BaSO_4$, and is weighed in this Form.

Note 1.—If the solution contains a large amount of nitric acid, this will interfere with the precipitation. It must, therefore, be removed by evaporation with HCl before the sulphate is precipitated by $BaCl_2$.

Note 2.—This estimation need not be repeated here, if it has been already carried out in Part I.

Weigh out about 1 gram of pure recrystallised $CuSO_4.5H_2O$ (Exp. 21, **80**) into an 18-oz. beaker. Dissolve this in about

100 c.c. of distilled water, containing a little dilute HCl, and heat the solution to boiling. If about 20 c.c. of strong ammonium chloride solution is added at this stage, the precipitate of $BaSO_4$ formed hereafter will be granular, and will therefore subside rapidly and be more readily filtered.

To the boiling $CuSO_4$ solution add excess of boiling $BaCl_2$ solution, and allow the liquid to stand until the white precipitate has subsided. Pour off the supernatant liquid through a filter, taking care not to disturb the precipitate. Wash the precipitate twice by decantation through the filter, and finally transfer it to the filter. Wash the precipitate until the last few drops of the wash-water give no turbidity with $AgNO_3$ solution.

Dry the filter with the precipitate and ignite the precipitate apart from the filter (**74–78**), preferably in a platinum crucible.

Before igniting the precipitate detach it *as completely as possible* from the filter. Then ignite the precipitate and the filter-ash together for about fifteen minutes at a dull red heat, allow the crucible to cool, and weigh it. These operations must be repeated until the weight is constant.

Any $BaSO_4$ which is left adhering to the filter-paper will be reduced to BaS during the incineration of the filter, and if BaS is produced in any appreciable quantity it will lead to error. The BaS must therefore be converted into $BaSO_4$ by the following procedure. The filter-ash, which has been dropped into a separate part of the crucible, is moistened with two drops of dilute HCl and then a drop of dilute H_2SO_4 is added. The contents of the crucible are then very gently heated until the liquid has been evaporated, great care being taken to avoid loss by spirting. The crucible and its contents are then strongly ignited, and are weighed after they have been allowed to cool.

From the weight of the $BaSO_4$ thus obtained, the percentage of SO_4 may be calculated.

Estimation of (SO_4) in an Insoluble Sulphate.

97. If the Sulphate is Insoluble in Water and in Acids it must be decomposed by fusion with alkaline carbonates. The following example will illustrate this process.

Weigh out accurately about 1 gram of pure finely-powdered $BaSO_4$ into a platinum crucible ; add to it about 6 grams of finely-powdered fusion mixture ($Na_2CO_3 + K_2CO_3$). Mix the substances in the crucible by stirring them with a thin glass rod rounded at its end. Then heat the covered crucible over a small Bunsen-flame, which is gradually increased in size until the alkaline carbonates begin to fuse. Now change the position of the crucible lid until a slight opening is formed, through which the progress of the fusion can be watched, and so adjust the flame that the alkaline carbonates remain in a fused condition for at least ten minutes.

Complete the process by heating the crucible over the blowpipe, and cool it rapidly by placing it upon a mass of iron. Then lay the crucible on its side in a porcelain dish or beaker, and allow it to stand in cold distilled water until the mass can be readily detached by a glass rod. This process may be hastened by boiling the water.

Then remove the crucible by a clean pair of tongs, and carefully rinse it into the solution with the wash-bottle. Crush any solid particles which remain, filter the liquid, and wash the $BaCO_3$ upon the filter with boiling water, until the washing-water gives no alkaline reaction. Mix the filtrate and washings, and acidify them with dilute HCl, guarding against loss by effervescence (44).

Then precipitate the sulphate as $BaSO_4$, as is directed in paragraph 96.

Estimation of Barium in its Soluble and Insoluble Compounds.

The Barium is precipitated from solution as Barium Sulphate, and is weighed as such (See 96, *Note* 1).

98. Barium Compounds which are Soluble in Water or Acid.— Weigh out accurately about 1 gram of pure recrystallised barium chloride ($BaCl_2.2H_2O$) into an 18-oz. beaker, and dissolve it in 100 c.c. of water, to which some dilute hydrochloric acid has been added.

Heat the solution to boiling, and add a slight excess of hot dilute sulphuric acid. Wash the precipitate by decantation ; filter, wash and dry the precipitate, and ignite it as was described under the estimation of sulphate (96).

From the weight of the $BaSO_4$ thus obtained, calculate the percentage of barium.

99. Barium Compounds, which are Insoluble in Acid, are first subjected to fusion with alkaline carbonates (97). The barium carbonate residue, which is left upon the filter, after the fused mass has been extracted with water, is transferred to a beaker. This may be effected by pushing a hole through the filter with a glass rod, and then rinsing both rod and filter with the stream from the wash-bottle.

Dilute HCl is then poured through the filter into the beaker, and dissolves the $BaCO_3$ still adhering to the filter as well as that in the beaker. The filter is then washed well, the washings being allowed to flow into the beaker. The solution is finally precipitated, and the weight of the $BaSO_4$ is determined, as is directed in the second paragraph of 98.

The weight of Ba is then calculated from the weight of $BaSO_4$.

Estimation of Strontium in its Soluble and Insoluble Compounds.

100. The Strontium is precipitated from solution as Strontium Sulphate, and is estimated as such.

Weigh out accurately about 1 gram of pure precipitated strontium carbonate, $SrCO_3$ (82, Exp. 24), into a covered 18-oz. beaker. Dissolve it in a little dilute HCl, and add about 100 c.c. of distilled water. Add dilute sulphuric acid in excess, and then a quantity of methylated spirit about equal in volume to the liquid in the beaker. Allow the liquid to stand until the precipitate has subsided; then filter, and wash the precipitate with methylated spirit until the washings give no precipitate with $BaCl_2$ solution. Dry the precipitate in the steam-oven, and ignite the precipitate as was described under the ignition of $BaSO_4$ (96).

From the weight of $SrSO_4$ thus obtained, the percentage of strontium may be calculated.

101. Strontium Compounds which are Insoluble in Water, are dissolved in acid if possible (98), and the solution is treated as is directed above (100).

Strontium Compounds, which are Insoluble in Acid, are fused with alkaline carbonates (97). The residue, which is insoluble in water, is dissolved in HCl (99), and the Sr is precipitated as is directed above (100).

Estimation of Sulphur in Sulphides.

102. The Sulphide is converted by a suitable Oxidising Agent into Sulphate, and the Sulphate is precipitated and estimated as Barium Sulphate, $BaSO_4$.

From the weight of $BaSO_4$ obtained, the weight of sulphur, which was originally present as sulphide, is calculated.

The choice of the oxidising agent to be employed will depend upon the nature of the sulphide which is to be oxidised. Three methods are described below.

The First Method (**103**) is applicable to sulphides in solution.

The other Methods are used for solid insoluble sulphides. The Second Method (**104**) is more convenient and more generally applicable than the Third (**105**).

103. Oxidation by Bromine.—The solution of sulphide may be oxidised by adding bromine-water free from sulphuric acid (see *Note* below), and then gently warming the liquid.

The colour of the bromine disappears as it produces oxidation, and the bromine-water must therefore be added until the warm liquid retains its colour for about ten minutes. The liquid is then boiled until the bromine has been expelled, and the sulphate is precipitated by $BaCl_2$, as is directed in par. **96**.

Note.—Bromine is freed from sulphuric acid by careful redistillation, and is shaken with water until the water is saturated. This bromine-water should be tested for sulphuric acid by $BaCl_2$.

104. Oxidation by Sodium Peroxide.—Weigh accurately about 1 gram of very finely-powdered zinc-blende into a platinum or nickel crucible (see *Note*). Mix it very intimately in the crucible with about 6 grams of the sodium peroxide in very fine powder; and heat the covered crucible by supporting it about 2 inches above a small Bunsen-flame.

The mass will glow throughout, and will then settle down

in the fused condition. Allow the mass to remain fused for three minutes; and extract it, when it is cool, with water (97), taking precaution against loss of liquid which might arise from the effervescence caused by the evolution of oxygen (44). Neutralise the greater part of the NaOH, if the liquid is strongly alkaline; filter the liquid if necessary, acidify the clear solution with hydrochloric acid, and precipitate the sulphate by barium chloride solution (96).

Note.—Some samples of the peroxide contain metallic sodium; this alloys with platinum and spoils the crucible. It is well to try heating the peroxide in the flame on platinum foil before it is heated in a crucible.

It should be remembered that the peroxide must not be brought into contact with inflammable substances or with water.

105. Oxidation by Nitric Acid.—Weigh out accurately about 1 gram of very finely-powdered zinc-blende free from lead, into a 10-oz. flask. Introduce into the neck of the flask a small funnel to prevent loss by spirting during solution (fig. 28, p. 40): and pour upon the powder some red fuming nitric acid of specific gravity 1·5. When the action has somewhat abated, heat the flask in the water-bath. Continue to heat until the sulphur, which may separate at first, has dissolved. If necessary, use more acid to effect this end.

Then carefully transfer the liquid to a porcelain-dish, add a little sodium chloride to convert the free sulphuric acid into non-volatile sodium sulphate, and evaporate the liquid to a small volume over the water-bath.

Remove the nitric acid by repeatedly evaporating the solution to dryness with strong hydrochloric acid; and as soon as the nitric acid has been expelled, dilute the liquid with much water, precipitate the sulphate with $BaCl_2$ solution, and weigh the $BaSO_4$ thus formed (96).

Since the composition of Zinc-blende is variable, and the mineral is seldom pure ZnS, the theoretical percentage of sulphur required by the formula ZnS is rarely found. The accuracy of the analysis must therefore be determined by making a duplicate determination, since the result obtained cannot be checked by calculation of the theoretical percentage of S present in ZnS.

A Volumetric Method for estimating H_2S will be found in paragraphs **284–286**; another method depending on the evolution of H_2S is described in **462.**

Estimation of (SO_3) in a Sulphite.

106. The Sulphite is converted into Sulphate by the addition of Bromine-water, and is estimated as Barium Sulphate, $BaSO_4$.

Weigh out accurately about 1 gram of crystallised sodium sulphite, $Na_2SO_3.7H_2O$, into an 18-oz. beaker. Dissolve it in about 100 c.c. of water, containing a little dilute HCl. Then add bromine-water free from sulphuric acid (**103**, *Note*), until the liquid remains distinctly yellow in colour. Cover the beaker with a clock-glass and boil the liquid until the bromine is expelled.

To the colourless liquid add $BaCl_2$ in excess, and weigh the $BaSO_4$ precipitate in the manner already described in paragraph **96.**

From the weight of $BaSO_4$ thus obtained, the percentage of (SO_3) may be calculated.

107. Sulphites which are Soluble in Water may be treated at once by the above process.

Insoluble Sulphites may be decomposed by boiling them with sodium carbonate solution. The solution containing the sulphite as sodium sulphite is then filtered and is treated as is described above.

A Volumetric Process for estimating Sulphurous Acid is given in pars. **287, 288.**

Estimation of (S_2O_3) in a Thiosulphate.

108. The Thiosulphate is converted into Sulphate by Bromine-water, and is estimated as Barium Sulphate, $BaSO_4$.

For practice in this process about 1 gram of recrystallised sodium thiosulphate, $Na_2S_2O_3.5H_2O$, is accurately weighed and is dissolved in water. Bromine-water, free from sulphuric acid (**103**, *Note*), is then added until the solution remains yellow in colour, and the liquid is heated until the sulphur, which is precipitated, redissolves. The excess of bromine is then removed by boiling the liquid, and the sulphate is estimated as is described in paragraph **106.**

From the weight of $BaSO_4$ obtained, the percentage of (SO_3) is calculated.

A Volumetric Process for estimating Thiosulphate is given in par. **289.**

Estimation of Calcium in its Soluble Compounds.

The Calcium is precipitated from the solution of the calcium salt as Calcium Oxalate, which is converted into either Carbonate or Oxide, and is weighed as such.

109. Weigh out accurately into an 18-oz. beaker not more than 1 gram of pure calcium carbonate (**82**, Exp. 24), or of Iceland-spar. Add water, and dissolve the substance in dilute hydrochloric acid, guarding against loss of liquid by effervescence (**44**). Dilute this solution with water until its volume is about 100 c.c.

Heat the liquid nearly to boiling. Then add a slight excess of ammonium hydrate solution, and finally add solution of ammonium oxalate in moderate excess. Allow the liquid to stand until the precipitate has subsided.

Note.—The precipitate of CaC_2O_4 usually takes a long time to settle, and passes through the filter. To obviate these inconveniences the method of precipitation may be altered as follows.

Make the liquid alkaline, and heat it to boiling. Then take away the flame and add gradually about 2 grams of finely-powdered *pure solid* ammonium oxalate, while stirring continuously; and again heat the liquid to boiling. On taking away the flame, the precipitate will subside in a few minutes.

As soon as the precipitate has completely subsided, pour off the liquid through a filter, taking care not to disturb the precipitate. Wash the precipitate in the beaker two or three times with hot water by decantation. Finally transfer the precipitate to the filter by means of a glass rod tipped with rubber tubing, and a wash-bottle with a fine jet. Continue to wash the precipitate on the filter, until the last few drops of the washing-water no longer render silver nitrate solution turbid. Then dry the filter and precipitate in the steam-oven.

110. *The Precipitate of Calcium Oxalate is now converted into Carbonate.* With this object it is transferred, as completely as possible, to a platinum crucible. The filter-paper is

burnt in a platinum-wire spiral (**74**), and the ash is allowed to drop into the crucible. The crucible is then covered with the lid and is heated very gently at first, but it is finally heated more strongly for about twenty minutes, the bottom of the crucible appearing only faintly red when it is shaded from direct light. The crucible is weighed, after it has been allowed to cool in the desiccator.

Note.—The burner represented in figs. 47, 48 (p. 62) will be found specially suitable for the above purpose, since by its means a low and uniform temperature is easily obtained. The platinum capsule shown in these figures may also advantageously replace the crucible.

After the crucible has been weighed, its contents should be moistened with strong ammonium carbonate solution. It is then dried in the steam-oven, heated again to faint redness for a few minutes, allowed to cool, and once more weighed. These operations must be repeated until the weight no longer increases by the treatment. The object of the above procedure is to insure the conversion into carbonate of any calcium oxide which may have been formed by heating the precipitate too strongly.

From the weight of $CaCO_3$ thus found, the filter-ash is subtracted, and the percentage of calcium may then be calculated.

III. *Conversion of the Calcium Carbonate into Oxide.*—If the weight of the calcium carbonate obtained by igniting the oxalate does not exceed one gram, the result of the above estimation may be controlled by weighing the calcium also as oxide. Indeed, if the original precipitate is small in amount, it may be at once converted into oxide and be weighed as oxide instead of as carbonate.

In order to convert the calcium carbonate into oxide, the crucible and its contents are heated to bright redness over the blowpipe-flame for fifteen minutes; they are then allowed to cool, and are weighed. The crucible is once more heated for five minutes in the same way, and is weighed again after it has cooled. These operations must be repeated as long as they cause the crucible and its contents to lose in weight. The weight of substance finally left in the crucible is that of the calcium oxide and the filter-ash.

From the weight of CaO thus found, the percentage of calcium may be calculated.

A Volumetric Method of Estimation for Calcium is given in pars. **271–273.**

Estimation of (C_2O_4) in a Soluble Oxalate.

112. The Oxalate is precipitated as Calcium Oxalate, either in neutral solution or in a solution rendered acid by acetic acid. The Calcium Oxalate is then ignited, and is weighed either as Carbonate or as Oxide.

Weigh out accurately about 1 gram of pure crystallised ammonium oxalate, $(NH_4)_2C_2O_4.H_2O$, and dissolve it in about 100 c.c. of water. Heat the solution to boiling, and precipitate the oxalate by adding a solution of calcium acetate in slight excess. Convert the precipitated calcium oxalate into carbonate or oxide by ignition, as has been described in the estimation of calcium (**109–111**).

From the weight of $CaCO_3$ or of CaO thus obtained, the percentage of (C_2O_4) is calculated.

A Volumetric Method of Estimation for Oxalate is given in par. 270.

Estimation of Chlorine in a Soluble Chloride.

113. The Chlorine is precipitated as Silver Chloride, AgCl, and is weighed as such.

Weigh out accurately not more than 0·3 gram of pure sodium chloride (**82**, Exp. 25), and dissolve this in about 100 c.c. of *cold* water in an 18-oz. beaker.

Add to the *cold solution* a little dilute nitric acid, and then *excess* of silver nitrate solution. Shield the precipitate from daylight as much as possible during the whole of the estimation, since AgCl suffers slight decomposition and loss of weight when it darkens in the light. Heat the liquid in the beaker for some time, taking care not to let it boil; this will cause the small particles of the AgCl to unite together into flocks.

Wash the precipitate in the beaker by decantation three times with hot water containing a little nitric acid; then transfer it to a filter, and continue the washing with water alone until the last few drops of the washing-water are not rendered turbid by the addition of a drop of hydrochloric acid.

Dry the precipitate in the steam-oven, and ignite it apart from the filter in a *porcelain* crucible by one of the three following methods (**114, 115, 116**).

From the weight of silver chloride obtained, the percentage of chlorine is calculated.

114. *First Method.*—The precipitate is detached from the filter-paper as completely as possible, and is placed in a porcelain crucible. The filter is then folded and rolled up, carefully keeping the small portion of adherent precipitate in the *centre* of the roll (**74, 75**). The filter is then supported by a coil of platinum wire, and is incinerated in the usual manner.

During the incineration of the filter, metallic silver is always formed. This will alloy with the platinum, if it comes in contact with the red-hot wire, causing a loss in the weight of the AgCl found. This explains the necessity of keeping the precipitate from contact with the wire during incineration. The above risk is satisfactorily avoided by employing one of the methods described in pars. **77, 78.**

The filter-ash is added to the precipitate in the crucible, and the metallic silver in the ash is converted into chloride by moistening the ash with two drops of strong nitric acid, then adding two drops of hydrochloric acid, and evaporating cautiously to dryness.

The crucible is then gently heated over a small Bunsen-flame, until the silver chloride begins to fuse at its edges. It is then allowed to cool in the desiccator, and is weighed. If the amount of the chloride is large, the ignition should be repeated until the weight becomes constant.

115. *Second Method.*—The method described in par. **78** is well suited for the ignition of this precipitate, since the silver chloride is readily transferred without loss from the filter to the crucible.

The dry precipitate is turned out upon a piece of glazed paper, and is covered with a funnel. The filter is then folded and held in the flame by means of the crucible tongs;

the ash thus produced is allowed to drop into the crucible. The removal of any unburnt carbon from the ash is completed by burning it in the crucible. The ash may then be treated with nitric acid and with hydrochloric acid, and be dried by evaporation. The precipitate is finally transferred to the crucible and is ignited with the ash.

116. *A Third Method* of igniting the precipitate and burning the filter is described under the estimation of bromide, which follows in paragraph **118.**

117. Removal of AgCl from the Crucible.—After the determination has been finished, the silver chloride may be detached from the crucible as follows. Place on the cold mass a few pieces of granulated zinc; and then cover the whole with a layer of dilute sulphuric acid. The silver chloride will become partly reduced to metallic silver, and may then be easily detached. Place the filtrates, washing-water, and precipitate in the silver-residue bottle after the analysis is completed.

Two Volumetric Methods of Estimation for chloride are given in pars. 301–303.

Estimation of Bromine in a Soluble Bromide.

118. The Bromine is precipitated as Silver Bromide, AgBr, and is weighed as such.

Weigh out accurately about 0·5 gram of pure sodium bromide, NaBr, and proceed to estimate the bromine it contains as is directed for the estimation of chlorine in a chloride (**113**).

The following special method of weighing the filter-ash may, however, be substituted, since hydrobromic acid solution is rarely kept in the laboratory.

Transfer the precipitate from the filter to a porcelain crucible as completely as possible, and ignite it in the same manner as has been already described for the chloride (**114**). Allow the crucible to cool, and weigh it.

Incinerate the filter in a coil of platinum-wire (**74**), allow the ash to fall into the weighed porcelain crucible containing the precipitate, and weigh it again. The increase of weight of the crucible after the ash has been added, less the weight of the filter-ash, will give the weight of metallic silver which has been formed from the AgBr adherent to the filter-paper.

Almost the whole of the precipitate is thus weighed as AgBr; and

the weight of the portion which has been converted into metallic silver is calculated from the weight of silver found. This weight is added to the weight of AgBr already obtained, and thus the total weight of AgBr is found.

From this weight the percentage of bromine is calculated.

Estimation of Iodine in a Soluble Iodide.

119. The Iodine is precipitated as Silver Iodide, AgI, and is weighed as such.

Weigh out accurately from 0·5 to 0·8 gram of pure potassium iodide, KI. Proceed to estimate the iodine it contains, in exactly the same way as was described for the determination of chlorine in a chloride (**113**).

The silver iodide, adhering to the filter, is *not* reduced to metallic silver during the incineration of the filter, as is the case with the chloride and bromide. At a high temperature, however, silver iodide undergoes appreciable loss by volatilisation. Care must therefore be taken to detach the precipitate as completely as possible from the filter, and to ignite the silver iodide at a low temperature.

From the weight of AgI obtained, the percentage of iodine is calculated.

A Volumetric Process of Estimation for iodide is given in pars. 301–303.

Estimation of (ClO_3) in a Soluble Chlorate.

120. The Chlorate is converted by a suitable Reducing Agent into Chloride, and is estimated as Silver Chloride (113).

Weigh out accurately about 0·5 gram of pure recrystallised potassium chlorate, $KClO_3$, into an 18-oz. beaker. Dissolve the salt in about 100 c.c. of water, and add a slight excess of solution of lead nitrite, which has been prepared as is described below (**121**).

The presence of the nitrite in excess can be ascertained by mixing a drop of the liquid with solution of metaphenylene-diamine and adding a drop of sulphuric acid, when a reddish-brown coloration should be produced on standing.

Acidify the liquid with nitric acid, and heat it gently.

Precipitate the chloride, which is thus produced, with silver nitrate as AgCl, and estimate the AgCl as has been described in paragraph **113**.

From the weight of AgCl thus obtained, the percentage of (ClO_3) is calculated.

121. *Preparation of Lead Nitrite Solution.*—Boil together in a beaker a mixture of one part of lead nitrate, one and a half parts of metallic lead, and fifty parts of water. The liquid first turns yellow, and finally becomes colourless. This solution is cooled rapidly by immersing the beaker in a vessel of cold water. Basic lead nitrite will precipitate as a white powder. Shake this powder up in water, and pass carbon dioxide through the solution until the basic lead salt is completely decomposed. Filter off the lead carbonate, and preserve the lead nitrite solution in a well-stoppered bottle.

A Volumetric Method of Estimation for chlorate is given in par. 298.

Estimation of (CN) in a Soluble Cyanide.

122. The Cyanogen is precipitated as Silver Cyanide, AgCN, and is weighed as such; or the AgCN is ignited, and the Ag is weighed.

Weigh out accurately about 0·5 gram of potassium cyanide, KCN, and dissolve it in about 100 c.c. of water in an 18-oz. beaker. Add excess of silver nitrate solution, and then acidify with dilute nitric acid. Allow the precipitate to settle in the cold. Then treat the precipitate in one of the following ways:—

(a). Wash the precipitate on a tared filter (61), and dry it at 100° in the air-oven until the weight is constant. From the weight of the AgCN thus obtained, the percentage of cyanogen may be calculated.

(b). Wash the precipitate on an untared filter; dry it in the steam-oven; ignite the filter in a *porcelain* crucible, and then add the precipitate (78). Heat the crucible again over the Bunsen-flame and weigh it, and repeat the ignition until the weight becomes constant. From the weight of metallic silver which remains, the percentage of cyanogen can be calculated.

Note.—Commercial potassium cyanide is not pure, and varies in composition; hence the theoretical percentage weight of cyanogen corresponding to KCN will not be obtained in this determination unless chemically pure cyanide is used.

A Volumetric Method of Estimation for cyanide is given in par. 305.

Estimation of Silver in its Soluble Compounds.

123. The Silver is precipitated as Chloride, and is weighed as such.

Weigh out accurately about 1 gram of pure recrystallised

silver nitrate, $AgNO_3$, and dissolve it in about 100 c.c. of cold distilled water; then add a small quantity of dilute nitric acid.

To this solution add dilute hydrochloric acid, with constant stirring, and in slight excess. The presence of HCl in excess may readily be ascertained, since the precipitate subsides rapidly, leaving the liquid clear above it. Hence it is easily seen whether the addition of another drop of HCl causes any further precipitate.

Boil the liquid containing the precipitate for a short time; then decant the liquid, and wash the precipitate three times by decantation (53) with boiling water containing a little HNO_3. Transfer the precipitate to the filter, and finish washing the precipitate on the filter with water acidified with HNO_3, and finally with hot water only.

As soon as the washing-water is shown to be free from chloride, by remaining clear when it is tested with $AgNO_3$ solution, the filter and precipitate are dried in the steam-oven. The precipitate is then ignited in a porcelain crucible, apart from the filter, in the manner described under the estimation of chlorine (113).

From the weight of silver chloride thus obtained, the percentage of silver can be calculated.

Volumetric Methods of Estimation for silver are given in pars. 301–303.

Estimation of Lead in its Soluble Compounds.

124. The Lead may either be precipitated as Carbonate, which is converted by ignition into Oxide, and is weighed as such (125); or the Lead may be precipitated as Sulphate, and weighed as such (126).

125. Estimation of Lead by precipitation as Carbonate, and conversion into Oxide, PbO.—Weigh out accurately about 1 gram of crystallised lead acetate, $Pb(C_2H_3O_2)_2.3H_2O$, and dissolve it in about 100 c.c. of distilled water, containing a little acetic acid. Add ammonium carbonate solution, con-

taining a small quantity of AmHO, in *slight* excess, and warm. Addition of the ammoniacal salt in large excess must be avoided, since this would redissolve some of the precipitate which is formed.

Wash the precipitate until it is free from alkali, and dry it in the steam-oven. Detach the dry precipitate from the filter-paper as perfectly as possible, and ignite it in a *porcelain* crucible. Since lead very readily alloys with platinum, the methods described in paragraphs **77, 78** will be found most suitable for the incineration of the filter.

After the filter has been burnt, moisten the ash with nitric acid, and remove the excess of acid by gentle evaporation. Now heat the precipitate and filter-ash to redness, to expel the carbon-dioxide completely from the precipitate, taking care not to fuse the residue of the lead oxide.

As soon as the weight becomes constant, after repeated ignition, the percentage of lead can be calculated from the weight of lead oxide found.

126. Estimation of Lead by precipitation as Lead Sulphate, and weighing the Sulphate.—Weigh out the lead acetate and dissolve it in water as is described above (**125**). Then add dilute sulphuric acid in slight excess, and mix with the liquid twice its volume of methylated spirit. Allow the precipitate to settle; filter, and wash the precipitate on the filter with methylated spirit until the sulphuric acid is removed.

Dry the precipitate in the steam-oven, and ignite it apart from the filter (**77, 78**). Then convert any lead sulphide or metallic lead which has been formed during the incineration of the filter, into sulphate, by treating the ash with a few drops of nitric acid and one drop of dilute sulphuric acid. Evaporate the excess of the acids, and finally ignite the residue. Then heat the crucible repeatedly to dull redness until its weight becomes constant.

From the weight of $PbSO_4$ thus obtained, the percentage of lead is calculated.

A Volumetric Method of Estimation for lead is given in par. **274**.

Estimation of Bismuth in its Soluble Compounds.

127. The Bismuth is precipitated as Carbonate, and is subsequently converted into Oxide by ignition and weighed as such.

Note 1.—It should be noted that neither chloride nor sulphate of bismuth must be present in a solution of bismuth which is to be estimated by this method, since these salts are converted into basic chloride or basic sulphate of bismuth, and these basic compounds are not decomposed by ammonium carbonate. A solution containing chloride, sulphate, or other salt of bismuth may be precipitated as sulphide; the sulphide is then dissolved by heating it with somewhat dilute nitric acid; this solution is filtered, if necessary, and is then precipitated by ammonium carbonate as is directed below.

Note 2.—In order to obtain a known weight of bismuth nitrate in solution for carrying out the process described below, pure bismuth oxide, Bi_2O_3, is ignited to redness until its weight is constant: about one gram of the oxide is exactly weighed, and is dissolved in a little dilute nitric acid.

Add water to the solution of bismuth nitrate, acidified with nitric acid (*Note* 2), until the volume of the liquid is about 100 c.c. Then add solution of ammonium carbonate in *very slight excess*, and heat for a short time. It is necessary to guard against the presence of a large excess of ammonium carbonate in the liquid, since the bismuth carbonate precipitate is distinctly soluble in this reagent. Filter, wash and dry the precipitate, and ignite it apart from the filter, as is described under the estimation of lead as oxide (**125**).

From the weight of Bi_2O_3 thus obtained, the weight of bismuth may be calculated.

Estimation of Zinc in its Soluble Compounds.

128. The Zinc is precipitated as Carbonate, and is subsequently converted into Oxide by Ignition and weighed as such.

Weigh out accurately about 1 gram of pure recrystallised zinc sulphate, $ZnSO_4.7H_2O$ (**80**, Exp. 21). Dissolve this in an 18-oz. beaker in about 150 c.c. of water. Heat the solution nearly to boiling, and add sodium carbonate solution in excess. Boil for a short time; allow the precipitate to settle, and wash it three times by decantation with boiling water; then filter, and finish the washing on the filter. The washing should be continued until the washing-water shows no alkalinity to test-paper, and gives no precipitate with $BaCl_2$ solution.

Dry the precipitate in the steam-oven, and ignite it apart from the filter (**74**), using a porcelain crucible.

To prevent reduction of the zinc oxide during the incineration of the filter, and consequent loss of zinc by volatilisation, the following precautions should be taken. The paper should be freed from the precipitate as far as possible. Before the filter is incinerated, it may also be wetted with strong ammonium nitrate solution and dried. It is then carefully incinerated at the tip of the flame in a coil of platinum wire, and the ash is added to the precipitate in the crucible.

The crucible and its contents are heated to redness over the Bunsen-flame until the weight becomes constant. It is necessary to guard against the flame playing into the interior of the crucible during the ignition, else reduction of the zinc oxide might occur, when zinc would be lost by volatilisation.

From the weight of ZnO thus obtained, the percentage of zinc may be calculated.

A Volumetric Method of Estimation for zinc is given in par. **307.**

Estimation of Manganese in its Soluble Compounds.

129. The Manganese is precipitated as Carbonate, and is converted by ignition into Mn_3O_4, and weighed as such.

Note.—A known weight of manganese in solution is most easily obtained by reducing a weighed quantity of pure potassium permanganate in solution by sulphurous acid.

Weigh out accurately about 1 gram of pure recrystallised potassium permanganate, $K_2Mn_2O_8$, into a large porcelain dish. Pour sulphurous acid solution upon the crystals, or, better still, pass sulphur dioxide gas into the aqueous solution, until the colour of the permanganate disappears, and any oxide of manganese, which forms, is redissolved. Then add sodium carbonate solution in excess.

Wash the precipitate first by decantation and then on the filter, until it gives no alkaline reaction to test-paper. Then dry the filter and precipitate in the steam-oven.

Mix together the filtrate and washing-water which always contain a little manganese, and evaporate the liquid to dryness in a platinum or porcelain dish. Then wash the insoluble hydrated oxide of manganese, which is present in the residue, with hot water on a separate filter, and dry it in the steam-oven.

Ignite both precipitates apart from the filters (**74**) in the same crucible, and remove the alkali, which is always carried down by the precipitate of manganese hydrate, in the following manner.

Turn out the precipitate and ash into an agate or small porcelain mortar, add hot water, and rub the precipitate with the pestle to insure thorough mixture of the solid with the water. Filter through a fresh filter; and wash the manganese oxide on the filter with hot water until *no sodium coloration* is given to the Bunsen-flame, when the last drop of the wash-water is evaporated and ignited in a loop of clean platinum wire. Then dry the precipitate and ignite it apart from the filter (**74**) at a bright red heat, taking care that the flame does not enter the crucible. Repeat the ignition until the weight is constant.

From the weight of the Mn_3O_4 thus obtained, the percentage of manganese is calculated.

Volumetric Methods for estimating Manganese Dioxide are given in pars. **294–296**; and a method for permanganate in pars. **264–266**.

Estimation of Magnesium in its Soluble Salts.

130. The Magnesium is precipitated as Magnesium Ammonium Phosphate ($MgNH_4PO_4.6H_2O$); this is converted by ignition into Magnesium Pyrophosphate, $Mg_2P_2O_7$, and is weighed as such.

Weigh out accurately about 1 gram of pure recrystallised magnesium sulphate, $MgSO_4.7H_2O$ (80), into an 18-oz. beaker. Dissolve this in about 50 c.c. of cold water, add AmCl solution, and then AmHO solution in excess.

The presence of AmHO in excess is necessary, since the precipitate is slightly soluble in pure water. If a precipitate forms on the addition of the AmHO solution, more AmCl solution must be added to redissolve the precipitate.

To the clear alkaline liquid add an excess of sodium phosphate solution, and stir the liquid vigorously with a glass rod tipped with rubber tubing. Take care that the rod does not touch the side of the beaker, as this would lead to deposition of the precipitate on the glass.

Filter, after the liquid has been allowed to stand at rest for twelve hours. This delay is recommended to insure complete precipitation of the double phosphate. But if the mixture of the solutions is made in a stoppered cylinder instead of in a beaker, and the mixture is at once vigorously shaken for five minutes, the precipitation is rendered complete without standing.

The precipitate is washed on the filter with AmHO solution. This is made by diluting one measure of AmHO solution, of 0·880 specific gravity, with three measures of water. The washing must be continued until a few drops of the washings, after being acidified with nitric acid, give no opalescence with silver nitrate solution.

The precipitate is now dried in the steam-oven, and is either ignited apart from the filter (74), as is directed under (a), or the filter and the precipitate are ignited together (b).

(a). The precipitate is detached as completely as possible

from the filter and is transferred to a platinum crucible. The filter is then incinerated in a coil of platinum wire, by heating it at first very gently, and finally exposing it to a red heat. The filter-ash is then dropped into the crucible.

The ash should contain no black spots, which are due to unburnt particles of carbon. These generally remain, because the precipitate has been fused by being too strongly heated at first: charred particles of the filter then become inclosed in the fused salt, and the carbon is consequently burnt with difficulty.

The crucible is now covered with the lid, and is heated very gently by the Bunsen-flame; it is then heated to redness, and finally to bright redness over the blowpipe-flame. It is finally allowed to cool in the desiccator, and is weighed. The ignited precipitate should be perfectly white, and the ignition should be repeated until it ceases to lose in weight.

(b). The precipitate may be wrapped up in the dry filter, and finally ignited at a red heat in a platinum capsule (**70**). The use of the blowpipe is unnecessary. The process will usually require about twenty minutes.

From the weight of $Mg_2P_2O_7$ thus obtained, the weight of Mg may be calculated.

Estimation of (PO_4) in a Soluble Phosphate.

131. The (PO_4) is precipitated as Magnesium Ammonium Phosphate, $MgNH_4PO_4.6H_2O$; this is converted by ignition into Magnesium Pyrophosphate, $Mg_2P_2O_7$, and is weighed as such.

Weigh out accurately about 1 gram of pure recrystallised sodium phosphate, $Na_2HPO_4.12H_2O$, into an 18-oz. beaker, and dissolve it in about 100 c.c. of water. Add sufficient ammonium hydrate solution to make the liquid smell slightly of ammonia, and then a slight excess of "magnesia mixture"

(132). Stir the liquid vigorously with a glass rod, which should not touch the interior of the vessel, and allow it to stand for at least twelve hours; or shake the liquid vigorously in a stoppered glass cylinder for five minutes, when precipitation will be complete. Then treat the precipitate in the manner described under the estimation of magnesium (130).

From the weight of $Mg_2P_2O_7$ thus obtained, the percentage of PO_4 may be calculated.

132. Preparation of "Magnesia Mixture."—Dissolve one part of crystallised magnesium sulphate in eight parts of distilled water. Dissolve in this solution two parts of ammonium chloride, and then add four parts of the strongest solution of ammonium hydrate (0·88 sp. gr.). Allow this mixture to stand for several days, and decant the liquid from any solid matter which has settled down. The clear liquid is used for the precipitation of phosphate.

133. Phosphates which are Insoluble in Water should be dissolved in dilute nitric acid. The solution, which must contain very little phosphate, is mixed with a large excess of solution of ammonium molybdate in nitric acid (449), and the liquid is allowed to stand in a warm place for some hours. The precipitate thus obtained is filtered, and is washed with water containing a little nitric acid. It is then dissolved in ammonium hydrate solution; and this solution is precipitated by magnesia mixture, as is described above (131).

A Volumetric Method for estimating Phosphate is given in par. 310.

Estimation of (AsO_4) in a Soluble Arsenate.

134. The (AsO_4) is precipitated as $Mg(NH_4)AsO_4.6H_2O$; this is converted by ignition into $Mg_2As_2O_7$, and is weighed as such.

Weigh out accurately about 1 gram of pure recrystallised sodium arsenate, $Na_2HAsO_4.12H_2O$, into an 18-oz. beaker. Dissolve the solid in 100 c.c. of cold water, add some ammonium hydrate solution, and then excess of magnesia mixture (132). Stir well, and allow the liquid to stand for twenty-four hours, or shake it vigorously for five minutes in a stoppered glass cylinder. Then filter, and wash the precipitate thoroughly with ammonium hydrate solution, as was described in the estimation of Mg (130). Finally dry it in the steam-oven.

Separate the dry precipitate as completely as possible from the filter, and place it on a sheet of glazed paper (**78**). Then saturate the filter with strong ammonium nitrate solution; dry it, and incinerate it in a porcelain crucible, heating gently at first, and gradually raising the temperature to a red heat.

As soon as the filter is completely incinerated, transfer the precipitate also to the crucible. Cover the crucible as is shown in fig. 44 or fig. 45 (p. 61), and heat the precipitate in a slow current of oxygen, which may be supplied from a cylinder of the compressed gas. Gradually raise the temperature to bright redness. Allow the crucible to cool, and weigh it. Repeat the heating in oxygen until the weight becomes constant.

From the weight of $Mg_2As_2O_7$ thus obtained, the percentage of AsO_4 may be calculated.

Note.—The above special procedure is necessary to prevent the occurrence of reduction and the consequent loss of As by volatilisation; it further serves to secure a residue of fixed composition.

Estimation of Sodium in Sodium Chloride.

135. The Sodium Chloride is converted into Sodium Sulphate, Na_2SO_4, by evaporation with H_2SO_4 and ignition, and is weighed as such.

Note.—This process is applicable to any sodium compound which leaves Na_2SO_4 only as a residue, after it has been evaporated with strong H_2SO_4 and then ignited.

Weigh out accurately about 1 gram of purified NaCl (**82**, Exp. 25) into a platinum crucible. Moisten this with as small a quantity of water as possible. Then cover the crucible, and add concentrated sulphuric acid drop by drop, quickly replacing the cover after each addition of acid.

When no further effervescence is caused on the addition of acid, the crucible and its contents are heated cautiously over a small Bunsen-flame. The crucible should be supported in an inclined position, and be almost covered by the lid, a small opening only being left to permit the fumes of the sulphuric acid to escape. The heat should be applied near the top of the crucible, to prevent the liquid from creeping up the sides of the vessel (fig. 50, p. 63).

The evolution of white fumes must occur, since this furnishes proof that the H_2SO_4 has been added in excess. As soon as the fumes cease to appear, the crucible should still be heated to redness for at least fifteen minutes. The crucible is then allowed to cool in the desiccator, and is weighed. The above processes should be repeated, heating for five minutes only, until two consecutive weighings are identical.

It will be noticed during the process of heating that the saline mass becomes pasty. This is due to the sodium bisulphate, which is first formed and which is fusible at a dull-red heat, changing to the normal sulphate, which is infusible at that temperature.

The change from bisulphate into normal sulphate may be accelerated by the introduction of a little powdered ammonium carbonate into the crucible, when it is faintly red hot. The lid is then replaced, and the crucible is strongly heated for a few minutes. This treatment should be repeated until the weight is constant.

From the weight of Na_2SO_4 thus obtained, the percentage of Na can be calculated.

Estimation of Potassium in Potassium Chloride.

Two methods of estimation are described. The potassium is either weighed as platino-chloride (**136**), or as sulphate (**137**).

136. The Potassium Chloride is precipitated as the Double Chloride of Platinum and Potassium, K_2PtCl_6, and is weighed as such.

Note.—This method is only applicable to those potassium compounds, which can be completely converted into potassium chloride, by evaporation with hydrochloric acid: since it is only as chloride that the potassium can be completely precipitated by $PtCl_4$ solution.

Weigh out accurately into a 4-inch porcelain dish about

0·25 gram of pure recrystallised potassium chloride (80). Dissolve this in a small quantity of water, and add a few drops of hydrochloric acid. Then add platinum chloride solution in such quantity, that it contains a weight of $PtCl_4$ at least three times as great as that of the KCl used; and evaporate the liquid on the water-bath, until a semi-solid crystalline mass is obtained.

It is absolutely necessary that the platinum chloride should be present in excess. This is readily seen to be the case, by the supernatant liquid being of an orange colour after it has been concentrated to a small bulk.

Proceed to treat the residue left by evaporation, according to one of the methods (a) or (b) described below.

(a). *First Method.*—Pour alcohol upon the residue. Gently shake the liquid round in the dish, so as to mix the contents uniformly together. Allow the precipitate to settle completely, and pour off the liquid through a tared filter (61). Repeat these operations twice; and finally transfer the undissolved double salt to the filter, by means of a small wash-bottle filled with alcohol. Continue to wash the precipitate upon the filter with alcohol until the washings are no longer coloured. Dry the filter and its contents at 100° C. until the weight of the filter and $2KCl.PtCl_4$ is constant.

(b). *Second Method.*—A somewhat quicker method of treating the precipitated double salt is to wash it with alcohol in the dish by decantation, until the alcohol is no longer coloured, decanting off the alcohol through an untared filter-paper. Care must be taken that as little as possible of the precipitate is poured off with the alcohol. The double salt, freed from the excess of $PtCl_4$, is now removed by means of an alcohol wash-bottle into a platinum crucible; it is then dried at 100° C., and weighed.

The filter, which will contain a little of the double salt, is then incinerated (74), and the ash is dropped into the crucible, which is again weighed. By deducting the weight of the filter-ash from the increase noted in the weight of the crucible, the approximate weight of platinum left by ignition

in the filter-ash is found. The weight of double salt equivalent to this is calculated, and this weight is added to that of the double salt already found in the crucible.

If the quantity of precipitate left on the filter is appreciable, the weight of KCl which remains unchanged in the filter-ash will introduce an error. The filter should in that case be ignited in a separate crucible ; the KCl is then washed out from the ash by hot water, and the dried residue is weighed. The true weight of the platinum in the ash is thus ascertained, and from it the weight of double chloride which contained it, is calculated and is added to that already found.

From the weight of the double salt, K_2PtCl_6, thus found, the percentage of K can be calculated.

137. Estimation of Potassium as Sulphate.—The process is precisely similar to that described in paragraph **135** for sodium compounds. It is only suitable for those potassium compounds which leave a residue of potassium sulphate, K_2SO_4, when they are evaporated with sulphuric acid and then ignited.

Estimation of Ammonium in its Compounds.

The Ammonia gas is driven off by heating the substance with caustic alkali solution, and is estimated either gravimetrically (**138**) or volumetrically (**139**).

138. The Ammonia is expelled by heating the ammonium compound with Sodium Hydrate Solution, and is absorbed in dilute HCl; the Ammonium Chloride thus produced is precipitated as the Double Chloride $(NH_4)_2PtCl_6$ by Platinic Chloride, and is weighed as such.

The General Description of the Process will be understood by reference to fig. 56. The weighed ammonium compound is introduced into the flask (*a*), the caustic alkali solution is allowed to drop upon it from the funnel (*b*). When the flask is heated, ammonia is evolved, and is absorbed by dilute acid in the flask (*h*); the tube (*n*) also containing glass moistened with dilute acid to prevent the escape of

traces of ammonia. The enlargement in the tube (*d*) prevents the acid in (*h*) from being sucked back into (*a*).

Description of the Apparatus.—A twelve-ounce round flask (fig. 56, *a*) is fitted with a rubber cork, through which passes a stoppered funnel-tube (*b*) of about 50 c.c. capacity. The lower end of this funnel-tube is drawn out to a fine point. Instead of a funnel, a 50 c.c. pipette may be used, the lower end of which is drawn out; the upper end being fitted with a piece of rubber tubing which can be closed by a screw-clamp, so as to prevent the liquid it contains from descending (fig. 57*b*, p. 117).

FIG. 56.

This flask is connected by a bent tube with a 50 c.c. pipette (*d*) by means of a rubber joint. Both the tube and the top of the pipette must be of the same diameter, and their ends must be brought into close contact within the joint. This pipette passes through a rubber cork which is fitted in the neck of a ten-ounce conical flask (*h*). The lower end of the pipette is drawn out to a fine point. Through the same cork a small absorption-tube (*n*), filled with broken glass, also passes.

The conical flask is filled to the depth of about half an inch with hydrochloric acid, made by diluting the strong acid with six times its volume of water. The acid is poured into the flask down the tube containing the broken glass, and the glass is

thus wetted with the liquid. The point of the pipette is adjusted so as to dip just below the surface of the acid. The apparatus should be screened, or placed in a fume-closet, in order to avoid side-draughts while it is being used.

Description of the Process of Estimation.—About 1 gram of $Fe(NH_4)_2(SO_4)_2.6H_2O$ (**81**, Exp. 28) is accurately weighed out, all crystals showing a yellowish tinge being rejected. The salt is introduced into the round flask (*a*), and is then dissolved in about 50 c.c. of water.

The bulb of the funnel-tube or of the pipette (*b*) is now filled with sodium hydrate solution, prepared by dissolving one part of NaHO in four parts of water. The rubber cork, bearing the funnel and connecting-tube, is then fitted into the flask, and is bound down with copper wire to the neck of the flask. The connection with the other flask (*h*) is then made by means of the rubber joint.

The contents of the round flask are now heated to incipient ebullition, and the NaHO solution is allowed to drop slowly into the flask, by gradually opening the stopcock of the funnel (*b*), or unscrewing the screw-clamp of the pipette.

As the ammonia gas is given off, it is absorbed by the acid in the conical flask (*h*), which is kept cool by being placed in a dish of water. The bulb of the pipette (*d*) prevents the acid from being sucked back into the heated flask (*a*) by the absorption of the ammonia; since, as soon as the bulb becomes partially filled with the acid, air passes up in bubbles through the pipette and restores the equilibrium. The point of the pipette, which is only just immersed in the acid at the commencement of the process, must be occasionally raised, since the volume of liquid in the flask increases during the operation.

As soon as all the NaOH solution has run from the funnel (*b*), the flame is raised, and the contents of the flask are kept boiling briskly for about twenty minutes.

The two flasks are now disconnected, and the lower flask (*h*) with its pipette and absorption-tube are rinsed out with water into a porcelain dish. Excess of platinum chloride

solution is added to the contents of the dish. The liquid is evaporated on the water-bath, and the $(NH_4)_2PtCl_6$ is estimated in exactly the same way as the corresponding potassium salt (**136**).

The Determination may be Controlled, by igniting the precipitate to redness, and weighing the metallic platinum which remains.

For this purpose the crucible, containing the double salt together with the filter or the filter-ash, is gently heated at first covered with the lid. The lid is then removed and the heat is gradually increased, care being taken to burn away the carbon of the filter-paper thoroughly. The contents of the crucible are finally heated to bright redness and the metallic platinum is weighed. The residual platinum does not require to be washed, since AmCl is volatile.

139. The Ammonia, expelled by heating the Ammonium Compound with Caustic Alkali Solution, is absorbed in a known volume of Standard Acid, and the excess of acid is determined by titrating the acid with Standard Alkali Solution.

Note.—This method of estimation by means of standard solutions is much more rapidly carried out than that described in par. **138**, but it should not be attempted until the student has acquired some knowledge of volumetric analysis.

The ammonia gas is evolved and absorbed in precisely the same way as has been described above (**138**). The gas is absorbed, however, in 100 c.c. of normal sulphuric acid (**236**), contained in the flask (*h*).

After the evolution and absorption of the gas is complete, the absorption-apparatus is rinsed out with water as in the preceding process, and the acid and washings are made up to 200 c.c. The well-mixed liquid is then transferred to a burette, and is titrated against 10 c.c. of normal soda solution, using either litmus or methyl-orange as an indicator. Two titrations should not differ by more than 0·1 c.c.

The Following Example will serve to illustrate this process and the method of calculation.

0·9912 gram of crystallised ferrous ammonium sulphate was weighed out. The ammonia was absorbed by 100 c.c. of normal sulphuric acid. After the absorption the liquid was made up to 200 c.c.

21·06 of this liquid neutralised 10 c.c. of normal NaHO.

$\therefore$ 200 c.c. would require $\frac{200 \times 10}{21 \cdot 06} = 94 \cdot 969$ c.c. of normal NaHO,

$\therefore$ the number of c.c. of H_2SO_4 neutralised by the NH_3 $= 100 - 94 \cdot 969 = 5 \cdot 031$.

And since each c.c. of acid corresponds to 0·018 gram of NH_4, the weight of NH_4 in the salt $= 5 \cdot 031 \times 0 \cdot 018 = 0 \cdot 09081$,

$\therefore$ the percentage of $NH_4 = \frac{0 \cdot 09081 \times 100}{0 \cdot 9912} = 9 \cdot 16$.

Another Method for estimating Ammonia volumetrically is given in par. 245.

Estimation of Carbon Dioxide in a Carbonate.

Three methods of estimation are described below.

By the first method (**140**) the carbon dioxide is weighed directly.

The second method (**141**) depends upon finding the loss of weight which the carbonate undergoes by the removal of its carbon dioxide.

The third method (**142**) measures the volume of CO_2 evolved by the carbonate when it is decomposed by an acid.

140. By Direct Weighing. The Carbon Dioxide gas is liberated by treating the Carbonate with an Acid; it is then absorbed by means of Soda-lime, and is weighed.

The General Description of the Process will be understood by referring to fig. 57. The carefully weighed carbonate is introduced into the flask (*a*), and is decomposed by acid from the pipette (*b*). The carbon dioxide passes through strong sulphuric acid in the glass-bulb apparatus (*d*), which serves to dry the gas and to measure the rate of evolution. The gas then passes through the tube (*e*), which contains pumice with copper sulphate to absorb any hydrogen chloride expelled by heat from the acid in the flask (*a*).

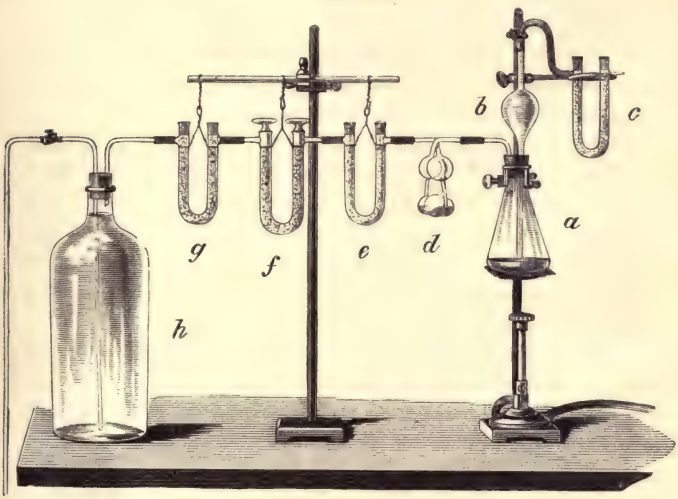
The carbon dioxide is finally absorbed by soda-lime in the weighed tube (*f*).

The tube (*g*) contains calcium chloride, and is intended to prevent water vapour from passing back from the aspirator to the tube (*f*). The aspirator-bottle (*h*) serves to draw air through the whole apparatus at the end of the process, so as to carry over all the carbon dioxide into the absorption-tube (*f*); the air is freed from carbon dioxide by passing through the soda-lime tube (*c*) on its way into the pipette (*b*) and the flask (*a*).

The tube (*f*) is weighed at the end of the process, and the increase of weight gives the weight of carbon dioxide evolved from the known weight of carbonate.

Description of the Apparatus.—The apparatus employed for this estimation is shown in fig. 57. An 8-oz. conical flask

FIG. 57.



(*a*) is fitted with a rubber cork bored with two holes. Through one of the holes passes a funnel-tube (fig. 56*b*), or a 50 c.c. pipette (fig. 57, *b*). This is filled with dilute acid for the decomposition of the carbonate, before the process

is started. The lower end of this pipette is drawn out to a fine point, which is situated about 1 inch from the bottom of the flask.

To the other end of the pipette is attached about 8 inches of rubber tubing, on which is a screw-clamp for opening or closing communication with the U-tube (*c*), which contains soda-lime. One end of this U-tube is connected with the rubber tubing, the other end being open to the air. This tube is intended to remove CO_2 from the air which is finally drawn through the apparatus.

A piece of bent glass tube is pushed through the other hole of the rubber cork in the flask (*a*) to the distance of about an inch. Attached to this tube are bulbs and U-tubes, connected with each other by rubber joints: these serve respectively for drying, purifying, and absorbing the carbon dioxide gas.

The bulb-tube (*d*) contains strong sulphuric acid: it serves for drying the gas, and also acts as a gauge to measure the rate at which the gas passes over from the flask (*a*). Liebig's or Geissler's potash-bulbs serve well for this purpose; the acid should half fill the three bottom bulbs.

The U-tube (*e*) has the limb nearest (*d*) filled with solid calcium chloride, which has been previously exposed to a slow stream of dry CO_2 to convert into carbonate any $Ca(OH)_2$ which it may contain. The other limb of this U-tube is filled with dehydrated copper-sulphate-pumice which absorbs the HCl which is given off during the heating of the liquid in flask (*a*).

The stoppered U-tube (*f*), which is the absorption-tube for the CO_2 evolved from the carbonate, has the limb nearest to the tube (*e*), the bend, and half the other limb filled with soda-lime, the remainder of the tube being filled up with solid calcium chloride. The soda-lime in this tube becomes heated when it absorbs CO_2, and any moisture which is thus expelled is absorbed by the calcium chloride, loss of weight by escape of moisture being thus prevented.

The remaining tube (*g*) is filled with solid calcium chloride, and in the figure is shown to be in connection with a water-

aspirator (*h*). The aspirator is connected with the tube only when the evolution of CO_2 has ceased; it serves to draw air through the flask and tubes at the end of the process, and this air serves to carry the CO_2 with it into the absorption-tube (*f*).

141. A Convenient Aspirator may be made from a Winchester quart-bottle (fig. 57, *h*). A sound cork bored with two holes is fitted into the neck of the bottle. Into one hole a piece of glass tube bent at right angles is fitted, the tube only just passing through the cork. Through the other hole passes a tube, also bent at right angles, but passing to the bottom of the bottle. When this bottle is to be used as an aspirator, a rubber tube, which extends below the level of the bench, is attached to the longer glass tube, so that this tube may act as a syphon. A screw-clamp on this rubber tube serves to regulate the flow of the water.

The bottle is now filled with water, and suction is applied to the syphon-tube until it is filled with water. A continuous stream of water will then continue to flow, by the action of gravity, after the suction is stopped. Air will supply the place of the water in the bottle, so that a continuous current of air can be aspirated through the series of tubes and flask, as soon as they are attached by rubber tube to the shorter tube in the bottle. The rate of aspiration can be regulated by the screw-clamp.

142. Preparation of the Absorption-tubes.—Fig. 58 represents a convenient form of U-tube for containing the solid absorbents. The tube should be first washed perfectly clean, and then rinsed with distilled water. It is then dried, either in the steam-oven, or more quickly by driving a current of air through it by means of a foot-bellows, and at the same time heating the tube gently over a Bunsen-flame.

FIG. 58.

When the absorbent is in the tube, it must always be protected from contact with the atmosphere. This is effected by pushing over the side-tubes short pieces of rubber tubing closed with little plugs of glass rod. These are only removed when the tube is being connected for use in the process of absorption, and while the tube is being weighed.

The granulated solid, which is used for filling the tube, must be freed from fine powder and large lumps. For since the solid particles absorb gas or vapour mainly by their surface, they should

be used as small as is admissible, so as to expose the largest possible absorbent surface. But fine powder must not be present, as this would fill up interstices and impede or even arrest the passage of the gas or vapour.

A suitable granular powder may be produced in the following manner. The solid is coarsely powdered in a porcelain mortar, and this powder is then shaken upon a perfectly dry and clean fine brass-wire sieve of twenty strands to the inch. The powder that passes through is rejected. The remainder is freed from large lumps by passing it through a coarser sieve of eight strands to the inch. The particles that pass through this sieve are used for filling the absorption-tubes. The larger pieces, which do not pass through this coarser sieve, are broken up again in the mortar, and are subjected once more to the above process of sifting.

The U-tube is filled with the granular solid up to the level at which the side-tubes enter. A loose plug of cotton-wool is then inserted, so as to prevent solid particles from being carried through the side-tubes by the gas current. Two sound corks of suitable size are softened by pressure, and are fitted into the open ends of the U-tube. Each cork is then cut off level with the top of the tube, and a little melted paraffin-wax is brushed over the cork so as to make it perfectly gas-tight.

The tubes (*c*) and (*g*) are filled in this way with soda-lime and with calcium chloride respectively.

The copper-sulphate-pumice, which (*e*) contains in addition to the calcium chloride, may be made in the following manner. Pumice-stone is granulated by powdering and sifting it in the manner described above. It is then heated with a moderately strong solution of copper sulphate. The liquid is poured off. The pumice, which is now saturated with the solution, is heated in the air-oven to a temperature of 200° C., until the blue colour of the copper-salt disappears. It may then be used for partially filling the tube (*e*) as has been already described.

143. Stoppered U-tube.—For the absorption-tube (*f*), either the U-tube shown in fig. 58, or a stoppered U-tube (fig. 57, *f*), which is more costly but more convenient, may be used. The stoppered tube differs from the one already described by having a hollow stopper ground into the upper part of each limb. These stoppers are wiped perfectly clean with filter-paper and are then greased with a little lard to make the tube air-tight. At the side of the hollow stopper, and on a level with the entrance of the side-tube, is a perforation ; so that

by simply turning the stopper round in its seat, communication between the U-tube and the side-tube may be opened or closed at pleasure.

It will be seen that by this arrangement the contact of the absorbent with the atmosphere may be prevented by simply turning the stopper. Therefore the caps for the side-tubes are unnecessary, and the process of weighing can be performed in the closed tube in a more leisurely fashion. Solid particles are prevented from being carried out of the tube by loosely filling the hollow stopper with a plug of cotton-wool.

144. *Testing the Apparatus.*—As soon as the tubes and flask have been connected by means of rubber tubing, the apparatus should be tested in the following manner to ascertain if it is gas-tight. To the last U-tube (*g*) is attached a piece of glass tube, which dips into a beaker of water. Gentle suction is then applied at (*c*) so as to cause the water to ascend about 6 inches in the tube attached to (*g*); the screw-clamp on (*b*) is then closed. If the level of the water in the tube remains unaltered for about ten minutes, the apparatus is air-tight.

If the level of the water in the tube, however, descends, the apparatus must admit air. The faulty rubber connection must then be found out, and the rubber must be bound upon the glass tube with fine copper wire. If this is insufficient, the rubber joint must be replaced by a new one.

145. *Description of the Process of Estimation.*—When the apparatus is sound, the estimation may be proceeded with as follows:—The absorption-tube (*f*) is first wiped clean and dry, and carefully weighed; it is then replaced in the series of U-tubes. About 1 gram of pure calcium carbonate (**82**, Exp. 24), or of Iceland-spar, is accurately weighed into the flask (*a*). The funnel-tube or the pipette (*b*) is then filled by suction with dilute hydrochloric acid (1 : 3), and the acid is kept in the pipette by closing the clamp at the top. The cork carrying the pipette is then inserted, and is bound down to the neck of the flask by means of thin copper wire. The aspirator (*h*) and the tube (*c*) are not attached until a later stage of the process.

The clamp above the pipette is now slightly opened, so as to let the acid drop slowly upon the calcium carbonate in the

flask. Carbon dioxide gas will slowly escape, and will drive out the air of the flask through the absorption apparatus. The bubbles should pass at such a speed through the acid-bulbs that they can be easily counted.

As soon as all the acid has flowed from the pipette into the flask the clamp above the pipette is closed, and the point of the pipette is carefully pushed down beneath the surface of the liquid in the flask.

The U-tube (*c*) and the aspirator are now attached; and the clamp above the pipette having been opened, the aspirator is slowly started into action. At the same time a small Bunsen-flame is placed under the flask, so as to maintain the liquid at incipient ebullition and expel the dissolved CO_2. The current of air, which is drawn through the apparatus by the aspirator, displaces the CO_2 gas from the flask, the bulbs, and the first U-tube, and carries it into the absorption-tube (*f*). The speed of the air-current is so regulated by means of the clamp attached to the aspirator, that the bubbles can be counted as they pass through the bulb-tube.

It will have been noticed that the soda-lime tube (*f*) becomes heated by the chemical combination of the CO_2 with the soda-lime during the early stages of the process. It cools again as absorption ceases, and air alone passes through it. Hence, when the absorption-tube (*f*) has become cold, most of the CO_2 gas is known to be absorbed. In order to insure complete absorption of the carbon dioxide, a volume of air, equal to about six times the capacity of the flask (*a*), should be drawn through the apparatus.

The stoppers of the tube (*f*) are then turned so as to close the side-tubes; or, if the ordinary U-tube has been used, the rubber stoppers are slipped upon the side-tubes. The U-tube is then disconnected, and is weighed after standing for about half an hour. The increase of weight it has undergone is the weight of CO_2 which was present in the weight of calcium carbonate taken.

From these weights the percentage of CO_2 in $CaCO_3$ can be calculated.

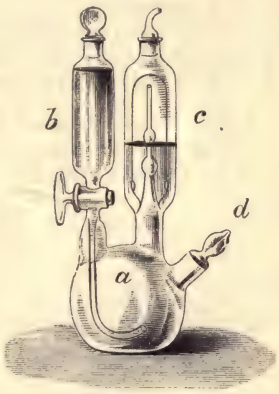
146. Estimation of Carbon Dioxide by Difference. The Carbon Dioxide gas is driven off by treating the Carbonate with an Acid, and the loss of weight, thus caused, gives the amount of Carbon Dioxide in the Carbonate.

This method is sometimes applied to the decomposition of a carbonate by dilute HCl or HNO_3. It is better suited for carbonates which are completely decomposed by H_2SO_4. When the more volatile acids are used, the results obtained are usually too high, owing to part of the acid being driven off when the liquid is heated at the end of the process.

Two forms of apparatus are described below for use in this process (**147**, **148**).

147. The Schrötter Apparatus, shown in fig. 59, is made of thin blown glass, so that its total weight does not exceed 50 grams.

FIG. 59.



Description of the Apparatus.—It consists essentially of a flask (*a*), in which the decomposition of the carbonate is effected. Communicating with this flask there are two reservoirs (*b*) and (*c*); also a stoppered opening (*d*), which serves for introducing the carbonate.

The reservoir (*b*) is filled with dilute acid. This may afterwards be introduced gradually into (*a*) by turning the stopcock, and serves to decompose the carbonate.

The reservoir (*c*) is half filled with strong sulphuric acid, which dries the CO_2 gas as it leaves the apparatus. The gas passes up through the vertical inner tube, then down again and out through the two holes at the base of the second tube. It then bubbles up through the strong sulphuric acid before making its escape through the upper exit tube into the air.

The Process of Estimation.—The proportion of CO_2 in pure sodium carbonate may be estimated by this method. The pure salt may be prepared by heating the pure bicarbonate in a platinum crucible to a dull-red heat, until it no longer loses weight by repeating the ignition. About 1 gram of this pure sodium carbonate is weighed with accuracy,

and is introduced into the apparatus through the opening (*d*). The receptacle (*b*) is then nearly filled with dilute sulphuric acid (1 : 5), and the receptacle (*c*) is half filled with strong sulphuric acid. The apparatus is then accurately weighed.

The dilute acid in (*b*) is now allowed to flow slowly into (*a*) by gradually turning the stopcock. As the acid attacks the carbonate, bubbles of gas will be seen passing through the strong acid in (*c*). The speed at which these bubbles pass must be so regulated, by adjusting the admission of the acid, that they can be easily counted. If they pass more rapidly than this, the gas will not be perfectly dried.

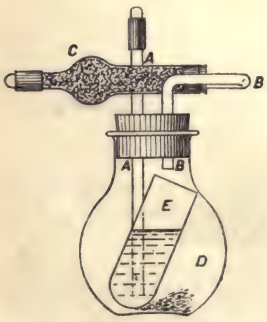
As soon as all the dilute acid has run into the flask, and the bubbles of gas no longer escape, the apparatus is placed upon wire-gauze on a tripod stand over a small Bunsen-flame. At the same time the aspirator (**141**) is attached by a piece of rubber tubing to the exit tube of (*c*), and a gentle current of air is drawn through the flask. The liquid in the flask is kept in a state of incipient ebullition, until a volume of air, equal to about three times the capacity of the flask and tubes, has been drawn through them. The flask is then allowed to cool, and is finally weighed. The loss of weight which it has suffered gives the weight of carbon dioxide in the sodium carbonate used.

This method is not suitable for very accurate analyses, as the results are usually too high. The error is due to the loss of water and acid during the heating and aspiration.

148. A Simple form of Apparatus, which may be fitted from materials which are available in any laboratory, is shown in fig. 60.

It consists of a light four-ounce flask with a short wide neck. A short doubly-perforated rubber stopper is fitted into the neck, and carries a tube, AA, which passes nearly to the bottom of the flask, and a small calcium chloride drying-tube, C. The external ends of these tubes are fitted with short pieces of rubber tubing, which are closed with small rounded glass rods.

FIG. 60.



The acid required for decomposing the carbonate is contained in a short tube, E, the length of which must be so adjusted that it stands obliquely in the flask without touching the stopper and without slipping into a horizontal position.

The procedure with this apparatus differs from that with the preceding apparatus (**147**) in several details.

As soon as all is ready for the decomposition, and the whole apparatus has been weighed without the caps, the cap is restored to the tube AA, and the acid is caused to flow slowly upon the carbonate by tilting the flask. When all the acid has been poured from the tube and the effervescence has ceased, the flask is warmed, and finally the cap of the tube AA is removed, and a slow stream of air is drawn by the aspirator (141) through the flask and drying-tube to displace the CO_2. The caps are then restored, and the apparatus is weighed again, without the caps, as soon as it is cold.

149. Estimation of Carbon Dioxide by measuring the Volume of Gas evolved by the action of an Acid upon the Carbonate.—The description of this method will be found under commercial gas analyses.

A Volumetric Method for estimating CO_2 in air is given in the section on Gas Analysis.

ESTIMATION OF (C_2O_4) IN AN OXALATE.

150. The Oxalate is mixed with Manganese Dioxide, and the mixture is heated with Sulphuric Acid. The CO_2 evolved is absorbed by Soda-lime and weighed. The weight of the CO_2 evolved is equal to that of the C_2O_4 in the oxalate.

The following equation represents the reaction :—

$$H_2C_2O_4 + MnO_2 + H_2SO_4 = 2CO_2 + 2H_2O + MnSO_4.$$

It must be remembered that free oxalic requires to be neutralised by AmHO before it can be estimated by this process.

The different forms of apparatus which are used in the estimation of CO_2 (figs. 57, 59, 60), may be used for this determination.

Weigh out accurately about 0·6 gram of finely-powdered pure ammonium oxalate, $(NH_4)_2C_2O_4.H_2O$, and intimately mix it with about three times its weight of finely-powdered manganese dioxide, which must be free from carbonate. (See *Note* below.)

Introduce this mixture into the decomposition flask. Use dilute sulphuric acid, and conduct the operation exactly as has been described above (140–148). The weight of the CO_2 evolved gives the amount of C_2O_4 in the oxalate taken, and from this the percentage of oxalate may be calculated.

Note.—The manganese dioxide used in this estimation must be carefully tested for traces of carbonate. If any carbonate is found, the oxide should be finely powdered and heated for about fifteen minutes with a little very dilute sulphuric acid. The oxide is then washed free from acid, and dried.

A Volumetric Method for the estimation of an oxalate is given in par. 270, and another **Gravimetric Method** is given in par. 112.

Estimation of Water, present in the Free and in the Combined State.

151. Three methods are described below for estimating the water adhering to, or chemically combined with a substance.

The first and second methods (**152**, **153**) are applicable to substances which lose all their water, but undergo no further change in composition, when they are heated. The water may be estimated in such cases by the loss of weight which the substance suffers when it is heated to a suitable temperature.

The third method (**154**) is generally applicable to all substances. But it must always be resorted to for substances which not only part with their water when they are heated, but also undergo further chemical change which causes alteration in their weight.

Instances of such substances are furnished by ferrous hydrate or ferrous carbonate, which undergo oxidation, and by precipitated carbonate of magnesia, which parts with carbon dioxide when it is heated. The water evolved on heating the substance is in such cases absorbed by a weighed desiccating agent, and is estimated by the increase of weight of the agent.

152. The Substance is dried by Heating it in a Steam-oven, and the loss of weight is estimated.

This Method is applicable to substances which lose their Moisture by being heated to 100° C., without undergoing further chemical change (**153**, *Note*).

Weigh out accurately about 2 grams of crystallised oxalic acid, $H_2C_2O_4.2H_2O$, between the weighed pair of watch-glasses with clip (fig. 8, p. 12). Then remove the upper glass and clip, and heat the lower glass containing the substance for about two hours in the steam-oven. Replace the upper glass and the clip, and weigh the whole after it has cooled in the desiccator.

Repeat the above processes of heating, cooling, and weigh-

ing, until two successive weighings give the same result. The water, which can be expelled at 100°, is then known to be completely removed; and its percentage amount may be calculated from the loss of weight which is suffered by the weight of substance taken.

153. The Substance is dried by Igniting it, and the loss of weight is estimated.

This Method is applicable to substances which lose all their Water at a temperature above 100° C., without suffering further chemical change.

This method is generally to be preferred to any other, on account of the rapidity with which it may be carried out.

Weigh out accurately about 3 grams of finely-powdered pure recrystallised barium chloride, $BaCl_2.2H_2O$, into a platinum crucible of known weight. Heat the covered crucible gradually over a small Bunsen-flame, slowly raising the temperature until the bottom of the crucible is at a dull-red heat. Keep the crucible at this temperature for at least fifteen minutes; then allow it to cool in the desiccator, and weigh it.

Repeat the above processes, heating for five minutes only, until two consecutive weighings are identical. The water, which can be removed by ignition, is then known to have been expelled; and its percentage amount may be calculated from the loss of weight which has been caused by heating the weighed substance.

Note.—In some cases the temperature of drying must be carefully regulated in order to avoid decomposition of the substance. An instance is given in paragraph **86.**

154. The Substance is Heated to a suitable temperature, and the Water-vapour is conveyed by a stream of gas into an Absorbent Substance, and weighed.

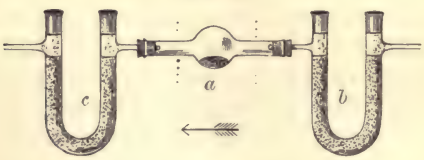
This Method is applicable to substances which lose their water when they are heated, but which also undergo further change of weight during the process, which is due to some other chemical change.

General Description of the Process.—The process will be understood by reference to fig. 61. The weighed substance is heated in a bulb-tube (*a*), which is connected at each end with a U-tube charged with a desiccating agent, preferably calcium chloride. The U-tube (*c*) is connected with a small washing-bottle containing strong sulphuric.

The air enters through the tube (*b*), passes over the substance in the bulb-tube, and leaves the apparatus after passing through the U-tube (*c*) and the wash-bottle. The air may be drawn through the apparatus by attaching an aspirator (**141**) to the wash-bottle connected with the tube (*c*). Or air may be driven through the apparatus by connecting a gas-holder with the tube (*b*).

The Apparatus is Fitted as is shown in fig. 61. A hard glass tube, of about $\frac{3}{8}$ inch bore and 6 inches in length, has a bulb about $1\frac{1}{2}$ inches in diameter blown in its middle (*a*).

FIG. 61.



The sharp edges of the ends of this tube are rounded by being held for a short time in the blowpipe-flame.

Two sound corks are softened by pressure, and are fitted air-tight into the ends of the bulb-tube; they are then perforated to receive the side-tubes of two U-tubes.

The U-tubes are filled nearly to the level of their side-tubes with granulated calcium chloride; cotton-wool plugs are then pushed into each limb, and the open ends are finally closed with sound corks. A full description of the fitting of the U-tubes and of the preparation of the calcium chloride will be found in pars. **142**, **143**. The side-tubes of each U-tube are then, if necessary, provided with little caps, made of rubber tubes closed with a piece of glass rod; and these

are only removed while the tube is in use or while it is being weighed.

When a high temperature is to be applied to the bulb by a flame, little discs of metal or of asbestos millboard should be slipped upon the bulb-tube, in the positions shown by the dotted lines in the figure, to shield the corks and prevent them from being scorched.

After the separate parts of the apparatus have been fitted together, it must be tested to ascertain if it is air-tight. For this purpose a short piece of rubber tube, carrying a screw-clamp, is pushed upon the free side-tube of tube (*b*), and by careful suction the sulphuric acid is raised several inches in the tube of the wash-bottle attached to (*c*). The rubber tube is then closed by tightening the screw-clamp. If the level of the acid does not fall in about ten minutes, the apparatus may be considered to be air-tight.

The Process is Carried out as follows:—The U-tube (*c*) is detached and is accurately weighed. The perfectly clean and dry bulb-tube (*a*) is then weighed.

About 3 grams of finely-powdered $BaCl_2.2H_2O$ are placed near the end of a little trough of stiff glazed paper, which will easily slip into the bulb-tube. This paper is pushed into the tube until the powder is within the bulb, and by rotating the bulb-tube or the trough on a horizontal axis the whole of the powder is deposited in the bulb. The paper trough is then removed, and the bulb is weighed again. Its gain in weight represents the weight of salt taken.

The whole of the apparatus is then fitted together again, and may be once more tested to see that it is air-tight.

An aspirator (**141**) is then attached by rubber tubing to the wash-bottle connected with the tube (*c*), and a slow stream of air is drawn through the apparatus, by adjusting the flow of water from the aspirator. The air must pass through the acid in the wash-bottle at such a rate that the separate bubbles can be easily counted. By this arrangement the air is dried by the calcium chloride in the tube (*b*) before it

passes into the bulb-tube. It then passes through the bulb-tube, and carries the water-vapour, which is expelled from the substance by heat, into the calcium chloride of the weighed U-tube (*c*). The wash-bottle guards the weighed U-tube from gaining weight by absorbing moisture, which might diffuse backwards from the aspirator. This bottle also serves as a gauge to measure the rate at which the air-current passes.

When the water is to be expelled from the substance at a known temperature, it is necessary to have the bulb-tube (*a*) bent in such a way, that the bulb can be immersed in a bath. The bath contains water or other liquid heated to the requisite temperature, which is shown by a thermometer dipping into it.

In the present example the bulb-tube may be heated by a small Bunsen-flame, as soon as the air-current through the apparatus has been adjusted.

The flame should be surrounded by the conical filter drier (fig. 43, p. 57), to prevent the absorption-tubes from being heated, and the corks and U-tubes may be further shielded by means of little metal discs, as has been already described.

The temperature of the bulb is gradually raised until it reaches dull redness, and the salt is heated in the air-current until no small drops of water remain on the cool part of the bulb-tube. The weighed U-tube (*c*) is then detached and reweighed; and from its gain in weight the amount of water in the weighed salt is ascertained.

From this result the percentage weight of water in crystallised barium chloride may therefore be calculated.

ESTIMATION OF CADMIUM IN ITS SOLUBLE COMPOUNDS.

155. The Cadmium is precipitated as Sulphide, CdS, and is weighed as such.

Weigh out accurately about 1 gram of pure recrystallised cadmium sulphate, $CdSO_4.4H_2O$. Dissolve it in about 250 c.c. of water, and add a few drops of dilute HCl.

Pass hydrogen sulphide (see Appendix) into this solution, until it smells strongly of the gas.

Filter off the CdS upon a weighed filter (**61**), and make certain that all the cadmium has been precipitated, by diluting a portion of the filtrate and passing H_2S through it again. If no further precipitation occurs, wash the precipitate first with dilute hydrogen sulphide solution mixed with a little HCl, and finally with pure water. Dry the filter containing the precipitate in the steam-oven, and weigh it (see **156**).

From the weight of CdS obtained, the percentage of cadmium may then be calculated.

156. This Precipitate frequently contains Free Sulphur. In accurate determinations, the dried precipitate should therefore be repeatedly washed with *recently distilled* carbon disulphide, as long as any residue is observed on evaporating a few drops of the washings upon a watch-glass. The precipitate is now again dried and weighed. Any loss it has undergone by being washed will be due to the removal of free sulphur.

Estimation of Antimony in its Solutions.

The Antimony is precipitated as Sulphide, Sb_2S_3, and is estimated either as such (157), or as the oxide, Sb_2O_4 (158).

Note.—If the quantity of antimony present is small, it should be weighed as Sb_2O_4, as is directed in par. **160.**

157. Precipitation as Sulphide, Sb_2S_3, and Estimation as such.—Weigh out accurately about 0·6 gram of anhydrous tartar emetic, $KHC_4H_3(SbO)O_6$ (**82**, Exp. 26). Dissolve this in about 200 c.c. of distilled water, and add a moderate quantity of tartaric acid solution and a few drops of dilute hydrochloric acid. If sufficient tartaric acid is not added, the antimony will be precipitated on the addition of the HCl or on dilution.

The clear liquid is transferred to an 18-oz. flask, which is fitted with a doubly perforated rubber cork. Through one of the holes in the cork passes a glass tube bent at right angles, which reaches to the bottom of the flask. Through the other hole passes a tube, one end of which terminates just below the cork, the other end being slightly contracted to hinder diffusion of air into the flask.

Hydrogen sulphide gas (see Appendix) is passed through the longer tube in a gentle stream into the liquid, until the liquid is saturated with the gas. The flask is then set aside for some hours in a *warm* place, to insure complete precipitation.

Carbon dioxide gas is next passed through the liquid until the excess of H_2S is removed. During the passage of the CO_2, the liquid is gradually heated to boiling; this renders the precipitate more dense and therefore more easy to wash.

Pour the liquid and precipitate upon a tared filter, dried at 100° (61). Filter with the aid of the filter pump, and wash the precipitate rapidly with hot water, containing a little hydrogen sulphide solution. During the washing of the precipitate, protect it against oxidation, by covering the funnel with a round glass plate.

Ascertain whether the precipitation of the antimony as sulphide is complete, by passing H_2S into the filtrate and washings, and then warming the liquid and allowing it to stand. If any further precipitate forms, add it to the main portion already on the filter.

When the precipitation and washing are complete, dry the precipitate in the steam-oven, until its weight becomes constant.

The precipitate will still contain water, and possibly free sulphur as well. Heat a little of the precipitate with strong hydrochloric acid. If it dissolves to a clear liquid, no free sulphur is present: proceed as is directed in par. **158**. If the liquid is turbid, free sulphur is present: treat the precipitate as is directed in par. **159**.

158. *In order to Remove the Water*, the greater part of the

dried precipitate is weighed in a tared porcelain boat. The boat is then introduced into a piece of combustion-tube about 9 inches in length, and a current of dry carbon dioxide gas (see Appendix) is passed over it. The boat is meanwhile gently heated with a Bunsen-flame, until the precipitate becomes black. The boat is then allowed to cool in the current of gas, and is finally weighed.

From the weight of the *anhydrous* Sb_2S_3 thus found, the total amount of the sulphide in the entire precipitate is then calculated, and from this result the percentage of antimony present can be ascertained.

159. *In order to Remove the Sulphur as well as the Water*, the precipitate is treated in the same manner as is described above (**158**), but the boat is heated to a higher temperature. The heating is continued until no more sulphur is volatilised.

The residue thus obtained consists of pure anhydrous Sb_2S_3, from which the percentage of antimony can be calculated.

160. Precipitation as Sulphide, Sb_2S_3, followed by conversion into Oxide, Sb_2O_4, and Estimation as such. —The antimony compound is precipitated in the form of sulphide, as has been already described (**157**). The sulphide is filtered off on a filter-paper which has been previously dried in the steam-oven and weighed (**61**). After the precipitate has been thoroughly washed, it is dried on the tared filter and weighed. The weight of the whole precipitate is thus obtained.

The precipitate is then transferred as completely as possible to a large weighed porcelain crucible, and the weight of precipitate thus transferred is ascertained by weighing it in the crucible. The precipitate is then moistened with several drops of strong nitric acid (sp. gr. 1·42): the crucible is covered with a watch-glass, and a quantity of fuming nitric acid (sp. gr. 1·5), sufficient to cover the precipitate, is quickly added from a pipette. For this purpose the cover is merely

slipped aside to admit the point of the pipette, since violent oxidation and frothing at once sets in.

The covered crucible is heated on the water-bath, as long as any further chemical action occurs. The cover is then removed, and the acid is evaporated by heating the crucible on the water-bath. The crucible is then removed, and is heated over the Bunsen-flame until the weight is constant.

From the weight of Sb_2O_4 thus found, the weight of Sb_2O_4 corresponding to the whole of the sulphide precipitate is calculated, and from this the percentage of antimony is obtained.

If the antimony sulphide contains much free sulphur, this must first be removed from the dried precipitate by means of carbon disulphide (**156**) before the treatment with nitric acid is carried out, else the action is so violent as to give rise to loss of substance.

It will sometimes happen that the amount of antimony sulphide on the filter is too small to be transferred to the crucible. If this is the case, the dried filter and precipitate are treated together in the crucible with about ten times their weight of the strong acid. The procedure is the same as that already described. In calculating the result, the filter-ash must be deducted from the weight of Sb_2O_4 obtained.

A Volumetric Method of estimating antimony is given in par. **281**.

Estimation of Arsenic in Solutions containing this Element in the Arsenious Condition.

Two methods of estimation are described below.

According to the first method, the arsenic is precipitated as As_2S_3, and is weighed as such.

According to the second method, the arsenic is precipitated as $Mg(NH_4)AsO_4.6H_2O$; this is converted into $Mg_2As_2O_7$ by ignition, and the arsenic is weighed in this form.

161. The Arsenic is precipitated as Arsenious Sulphide, As_2S_3, and is weighed as such.

Weigh out accurately about 0·6 gram of pure resublimed arsenious oxide (**83**, Exp. 28). Place the substance in an

18-oz. flask, and add about 50 c.c. of *dilute* hydrochloric acid. Heat the flask on a water-bath until all the solid is dissolved, care being taken that the temperature of the solution does not reach 100° C., else some of the arsenic will be volatilised as chloride.

If any As_2O_5 is present, a few drops of sulphurous acid solution are next added to convert the As_2O_5 into As_2O_3, and the flask is heated on the water-bath until all smell of SO_2 has disappeared.

The liquid is then considerably diluted, and the arsenic is precipitated as As_2S_3, by passing hydrogen sulphide gas through the solution in precisely the same manner as was described for antimony (**157**).

Carbon dioxide gas is then passed through the solution (**157**), until the smell of H_2S has almost disappeared. This tedious operation may be omitted, if great care is taken that the precipitate is kept covered, and is exposed as little as possible to the air during filtration.

The liquid is poured through a tared double filter which has been dried at 100° C., and the precipitate is washed with hot water containing a little H_2S, until it is free from hydrochloric acid.

The filtrate and washings are tested to make sure that all the As is precipitated, by saturating the liquid with H_2S gas, and allowing it to stand. If any further precipitate forms, this is added to the main portion on the filter. The precipitate is then dried at 100° C. in the steam-oven until the weight becomes constant.

Since the precipitate may still contain a little free sulphur, it should be treated with carbon disulphide (**156**). After this treatment the precipitate is again dried at 100°, and is finally weighed.

From the weight of the As_2S_3 thus obtained, the percentage of arsenic is calculated.

162. The Arsenic in the Arsenious compound is converted into Arsenic acid; this is precipitated as Mag-

nesium Ammonium Arsenate (134), $Mg(NH_4)AsO_4.6H_2O$; and this is converted by ignition into Magnesium Pyrarsenate, and is weighed as such.

Add strong HCl to the arsenious solution, heat gently, and add from time to time a crystal of potassium chlorate until the liquid smells strongly of chlorine. Allow the liquid to stand in a warm place until the smell of chlorine has nearly disappeared.

The solution now contains the arsenic as arsenic acid. It is made alkaline by the addition of ammonium hydrate, and the arsenic is completely precipitated by magnesia mixture (132). The precipitate is then ignited in oxygen (134), and is weighed as magnesium pyrarsenate.

From the weight of $Mg_2As_2O_7$ thus obtained, the percentage of As may be calculated.

A Volumetric Method for estimating arsenic is given in par. **282.**

Estimation of Tin in Solution of a Stannous or Stannic Compound, and of Metallic Tin.

163. The Tin is precipitated from solution as Sulphide, and this is converted by ignition in the air into the Dioxide, SnO_2, and is weighed as such.

Weigh out accurately about 1 gram of pure crystallised stannous chloride, $SnCl_2.2H_2O$, which has been kept in a well-stoppered bottle. Place the salt in an 18-oz. beaker, dissolve it in a small quantity of dilute hydrochloric acid, and make up the solution with distilled water to about 200 c.c.

Through this solution pass H_2S gas to saturation. Cover the beaker loosely with a filter-paper, and allow it to stand in a warm place until the smell of hydrogen sulphide has nearly disappeared. Transfer the precipitate to a double filter, and wash it until it is free from dissolved salts. Then dry and ignite the precipitate.

Since tin alloys with platinum, a porcelain crucible should be used, and one of the methods described in pars. 74–78 should be chosen for the ignition of the precipitate and the incineration of the filter.

Incinerate the filter-paper apart from the precipitate. Moisten the filter-ash with two drops of strong nitric acid, heat gently until the acid is expelled, and then raise the temperature to a red heat. Allow the crucible to cool; then add the precipitate, and after covering the crucible with the lid, heat it gently for some time. Then remove the lid, and heat gently until the smell of escaping sulphur dioxide is no longer perceptible, and finish by heating to bright redness over the blowpipe-flame.

To insure the complete removal of the sulphur allow the crucible to cool, add a little powdered ammonium carbonate, and heat again strongly. Repeat these operations until the weight remains constant.

From the weight of SnO_2 thus obtained, the percentage of tin is calculated.

A **Volumetric Method** for estimating stannous chloride is given in par. 283.

164. Metallic Tin is converted into Dioxide, SnO_2, directly, by heating the Metal with Nitric Acid and igniting the product.

The tin is oxidised by heating it in moderately strong nitric acid. Hydrochloric acid must not be present, else some tin chloride will be formed and will volatilise. As soon as all action has ceased, the solution is evaporated nearly to dryness on the water-bath, and is then diluted with water. The white SnO_2 is then filtered off, washed, and dried. The filter-paper is treated as is described in the preceding method (163). The SnO_2 is then added to the filter-ash in the crucible; and the whole is finally ignited over the blowpipe until the weight is constant.

Estimation of Mercury in its Compounds.

Two methods of estimation are given.

By the first the mercury is separated from a solid substance, and is weighed as metal.

The second method proceeds by precipitating the mercury as sulphide, and weighing the sulphide. It serves for solutions of mercury compounds, and for the separation of mercury from other metals in solution.

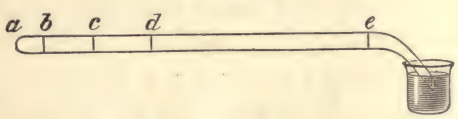
165. The Mercury Compound is decomposed by heating it with Calcium Oxide, the escaping Mercury vapour is condensed, and is weighed as metallic mercury.

Note.—This process is not applicable to mercuric iodide, which must be decomposed by heating it with metallic copper instead of with lime.

The process of estimation is conducted in the apparatus which is represented in fig. 62.

A piece of combustion-tube, about $\frac{3}{8}$ inch in internal diameter and about 18 inches in length, is closed by drawing it off at one end (*a*) in the blowpipe-flame.

Fig. 62.



Powdered magnesite is introduced into the clean, dry tube in quantity sufficient to form a layer 2 inches in length (*a*–*b*).

About 1 gram of pure mercuric chloride is then accurately weighed, and is mixed intimately with powdered quicklime in a porcelain mortar. This mixture is introduced into the tube (*b*–*c*), and the mortar is rinsed out with a little more quicklime, which is also transferred to the tube (*c*–*d*). The tube is then filled in with powdered quicklime to within

2 inches of its open end, the powder being kept in its place by pushing in a loose plug of asbestos (*e*).

The open end of the tube is now drawn out in the blow-pipe-flame; the narrow tube is bent obliquely, and its end is cut off as is shown in the figure. A passage along the whole length of the tube is formed by holding the tube horizontally, and tapping it gently upon the bench. The tube is then laid in a combustion-furnace upon an iron trough covered with asbestos; and the end of the bent tube is made to dip just beneath the surface of water contained in a small weighed beaker.

The front portion of the tube (*e*–*d*) is now gradually heated to redness. The heating is then slowly extended to that part of the tube which contains the mercury compound, and the heating is continued until the whole portion (*e*–*b*) is at a bright red heat. In this way the mercury is set free in the form of vapour, which is condensed to the liquid form as it passes into the water in the beaker.

The magnesite in (*a*–*b*) is finally heated to redness so as to produce a stream of carbon dioxide gas, which sweeps out the last traces of mercury vapour from the tube into the water.

While the tube is still red-hot, the narrow delivery tube is cut off at the bend by means of a cold file, and the mercury, which has condensed in this portion of the tube, is washed out and added to the main portion in the beaker.

The globules of metal are now united into one mass by gently agitating the contents of the beaker. The water is then poured off as far as possible, and a further portion is removed by absorbing it with filter-paper.

The mercury is finally rendered perfectly dry, by exposing it to the desiccating action of strong sulphuric acid under a bell-jar.

As soon as the weight of the metal remains constant, the percentage of mercury present in the original substance may be calculated.

166. The Mercury is precipitated as Sulphide, HgS, and is weighed as such.

Weigh out accurately about 0·5 gram of pure mercuric chloride into an 8-oz. beaker. Dissolve it in about 100 c.c. of water, add a few drops of dilute hydrochloric acid and pass hydrogen sulphide into the liquid until it is saturated. The colour of the mercury sulphide precipitate will become perfectly black as soon as the liquid is saturated with the gas.

Allow the precipitate a short time to deposit, then filter through a *tared* filter (**61**). Wash the precipitate quickly with cold water; dry at 100° C., and weigh it.

The precipitate may contain free sulphur. It should therefore be perfectly dried and washed with *recently distilled* carbon disulphide (**156**). The process of washing is repeated until the washings leave no residue on evaporation. The precipitate is then dried at 100° C. and weighed.

From the weight of HgS obtained, the percentage of Hg may be calculated.

ESTIMATION OF COBALT IN SOLUTION.

167. The Cobalt is precipitated as Hydroxide: the precipitate is dried and is then ignited in a current of Hydrogen gas, and is weighed as metallic cobalt.

Weigh out accurately about 1 gram of crystallised cobalt sulphate,* $CoSO_4.7H_2O$, into a porcelain or platinum dish. Dissolve this in about 100 c.c. of water, and heat the solution nearly to boiling.

Add to the boiling liquid pure potassium hydrate solution in slight excess, and heat the liquid until the precipitate becomes brown. Wash the precipitate with boiling water three times by decantation; transfer it to a filter, and continue to wash the precipitate until it is free from alkali. Dry the preci-

* This salt is efflorescent, and will therefore not give the percentage of cobalt required by its formula, unless it is freshly prepared.

pitate in the steam-oven, and ignite it together with the filter (73) in a porcelain crucible.

As soon as the incineration of the paper is complete, place either an inverted clay tobacco-pipe, or Rose's lid and tube, upon the crucible (figs. 44, 45, p. 61), and continue the ignition while a gentle current of pure dry hydrogen is passed through the pipe or tube.

The hydrogen gas is generated by the action of pure dilute sulphuric acid upon granulated zinc (see Appendix), or is supplied from a cylinder of the compressed gas. It must be completely dried by passing the gas through strong sulphuric acid.

The contents of the crucible are heated to dull redness in the stream of hydrogen for about fifteen minutes: and the metal is then allowed to cool in the current of the gas.

The residue of metallic cobalt is washed with boiling water, until it is free from the alkali which accompanies the precipitated hydrate. It is then dried and again ignited in hydrogen, and weighed. The ignition in hydrogen must be repeated until the weight becomes constant.

From the weight of metallic cobalt thus obtained, the percentage of cobalt in the compound may be calculated.

Estimation of (NO_3) in a Nitrate.

The estimation may be made by one of three methods.

By the first the solid nitrate is heated with excess of silica, and the loss of weight of N_2O_5 is ascertained. This method is less accurate than the other two.

By the second method the volume of NO, which is evolved when the solution of nitrate is shaken with mercury and strong H_2SO_4, is measured.

By the third method the nitrate is acted upon by nascent hydrogen, and the NH_3 thus produced is estimated.

168. The Solid Nitrate is heated with excess of Silica; the loss of weight gives the amount of nitric anhydride, N_2O_5, expelled from the nitrate.

Note.—From certain nitrates, such as $Pb(NO_3)_2$, the nitric anhydride may be expelled by simple ignition, an oxide of the metal remaining. In the case of most nitrates, however, such as those of the alkali-metals and of the alkaline-earth metals, it is necessary to heat the nitrate with silica, else the residue left after ignition is not of fixed composition.

Fuse a few grams of pure potassium nitrate in a porcelain crucible at as low a temperature as possible, and pour out the fused salt into a warm porcelain dish. Powder the solid mass while it is still warm, and place the powder in a stoppered weighing-bottle.

For practice in the process, weigh out into a platinum crucible about 2 grams of finely-powdered quartz or silica. Ignite this, allow it to cool, and weigh it. Add about 0·5 gram of the powdered potassium nitrate, prepared as described above, and weigh again, to ascertain the exact weight of the nitrate added. Mix the powders intimately and without loss by means of a glass rod rounded at the end.

Expose the crucible, covered with the lid, to a dull-red heat for thirty minutes; then allow it to cool, and weigh. Heat it again for ten minutes, and once more weigh. Repeat these operations until the weight becomes constant.

The loss of weight by ignition will be due to the total expulsion from the nitrate of the elements of N_2O_5. From this loss the percentage of NO_3 in the nitrate may be calculated.

169. The Solution of the Nitrate is decomposed by means of strong Sulphuric Acid in the presence of Mercury, and the volume of NO evolved is measured.—This method is described in the Section on Gas Analysis.

170. The Nitrogen of the Nitrate is converted into NH_3 by the reducing action of Al in contact with KHO solution, or by the Copper-Zinc Couple, and the NH_3 is estimated.—This method is described in the Section on Water Analysis.

Estimation of Silica in a Silicate.

171. The Silica is separated and is converted into the Insoluble Form by adding excess of acid to the Silicate and evaporating to dryness: the Silica is then rendered completely anhydrous by heat, and is weighed as SiO_2.

The method of procedure will vary according as the silicate can be decomposed by acid or not (**172, 173**).

172. If the Silicate is Soluble in Water, or can be Decomposed by strong Hydrochloric or Nitric acid, it is treated as is described below.

For practice in the estimation, weigh out accurately about 1 gram of finely-powdered "soluble glass," or sodium silicate, into a platinum or porcelain dish. Moisten the powder with water. Place the dish, covered with a clock-glass, upon the water-bath, and gradually add strong HCl, constantly stirring the contents of the dish with a glass rod rounded at the end.

As soon as the powder is completely decomposed, which is known to be the case when no gritty particles are felt with the glass rod, remove the cover, and continue the heating until the liquid is evaporated to dryness. Continually stir the residue, breaking up the lumps by means of the glass rod. When the powder appears perfectly dry, and no moisture is deposited on a cold clock-glass, when it is placed upon the dish for a few seconds, all the silica will have been separated in the insoluble condition.

As soon as the dish is cold, moisten the powder with strong hydrochloric acid, and warm the dish upon the water-bath. Then add hot water, stir well, allow the solid to subside, and decant the liquid through a filter. Repeat these processes of treatment of the residue three times. Then transfer the silica to the filter, wash it thoroughly with hot water, and dry it in the steam-oven.

The powder is now transferred to the crucible as com-

pletely as possible, and the filter is incinerated in a platinum-wire coil, and is added to the precipitate (74). The crucible is covered with the lid, and is gently heated. Care must be taken at this stage that none of the light, fine silica-powder is lost by being carried off with the escaping moisture. Gradually increase the temperature until the crucible reaches a bright red heat, and keep it at this temperature for fifteen minutes. When the crucible ceases to lose in weight by being heated, the percentage of SiO_2 may be calculated.

After the silica has been finally weighed, it should always be treated in the following way.

Heat the ignited silica in a platinum vessel on the water-bath with pure hydrofluoric acid and a few drops of strong H_2SO_4; evaporate to dryness, and ignite and weigh the residue. Repeat this process until no further loss of weight occurs. The total loss of weight by the treatment with hydrofluoric acid represents the weight of the silica.

From the weight of silica thus found, the percentage of silica may then be calculated.

173. If the Silicate is Insoluble in Acids and is not Completely Decomposed by Acid (389), it is finely powdered and is then fused with six times its weight of fusion mixture ($Na_2CO_3 + K_2CO_3$) in a covered platinum crucible for about fifteen minutes. The solid is then detached from the crucible by boiling it with ten times its weight of water for about half an hour in a covered evaporating dish. A little strong HCl is then added, and when nothing but gelatinous silica remains in the liquid, the contents of the dish are evaporated to dryness and the residue is treated as is described above (172).

Estimation of Fluorine in a Fluoride.

174. The Fluoride is precipitated as Calcium Fluoride, CaF_2, and is weighed as such.

Three methods of procedure are described. The first method serves for a neutral fluoride; the second method for a fluoride with acid reaction; and the third method for an insoluble fluoride.

175. Neutral Fluorides.—To the solution of the fluoride, contained in a platinum or porcelain dish, add an excess of calcium chloride solution, and heat the mixture to boiling. Allow the precipitate of calcium fluoride (CaF_2) to subside, and wash it twice by decantation. Then transfer the precipitate to the filter, wash it free from dissolved salts by means of hot water, and dry it in the steam-oven.

The precipitate and filter are ignited together (**73**) at a red heat, and are weighed.

From the weight of calcium fluoride (CaF_2) thus obtained, the percentage of fluoride can be calculated.

176. Fluorides with Acid Reaction.—The solution of the fluoride, contained in a platinum or porcelain dish, is mixed with sodium carbonate solution in excess. The mixture is heated to boiling, and is then filtered, if necessary. Calcium chloride solution is then added in excess. When the precipitate, which consists of a mixture of calcium fluoride and calcium carbonate, has subsided, it is washed first by decantation and finally on the filter. The precipitate is then dried and is ignited in a platinum crucible.

The ignited precipitate is now transferred to an evaporating dish, and is treated first with water and then with acetic acid in excess. The mixture is evaporated to dryness on the water-bath, and is ignited until it no longer smells of acetic acid. The residue, which consists of a mixture of calcium fluoride and calcium acetate, is washed with hot water until it is free from calcium acetate. It is then filtered, dried, and weighed, as is described above (**175**).

177. Insoluble Fluorides.—The finely-powdered fluoride is fused in a platinum crucible with about six times its weight of fusion mixture ($Na_2CO_3 + K_2CO_3$), until it is entirely decomposed. The cool mass is then dissolved by heating the crucible with water. The solution is filtered, if necessary, and is precipitated by the addition of calcium chloride solution in excess. The calcium fluoride in the precipitate is then estimated as is described above (**176**).

Estimation of (B_2O_3) in Crystallised Borax.

178. The Borate is Evaporated to dryness with Hydrochloric Acid: the Boric Acid-radicle is thus expelled, and is replaced by the chemically equivalent amount of Chlorine, which is estimated in the residue.

Weigh accurately about 1 gram of pure recrystallised borax ($Na_2B_4O_7.10H_2O$) into a porcelain dish. Add an excess of hydrochloric acid, and evaporate the solution to dryness on the water-bath. As soon as the liquid has been driven off, add a little more hydrochloric acid, and once more evaporate to dryness. Then heat the residue upon a sand-bath until no more acid fumes are given off.

Estimate the chlorine (**113**), and from this result calculate the amount of B_2O_3, assuming that Cl is equivalent to B_2O_3.

Estimation of (B_2O_3) in Boric Acid.

179. The solution of Boric Acid is mixed with a weighed quantity of pure anhydrous Sodium Carbonate in excess; the liquid is evaporated to dryness, and the Carbon Dioxide in the residual Carbonate is determined.

Weigh out accurately about 1 gram of pure crystallised boric acid, H_3BO_3, into a 10-oz. flask, and dissolve it in about 50 c.c. of water. Add about 3 grams of pure anhydrous sodium carbonate, transfer the liquid to a small weighed porcelain dish, and evaporate the solution to dryness. Heat the contents of the dish just to fusion, and maintain this temperature until effervescence ceases; then allow the dish to cool, and weigh it.

The residue in the dish contains a known amount of sodium oxide and an unknown amount of CO_2 and B_2O_3. Determine the CO_2 (**140**), and find the weight of the B_2O_3 by difference. The percentage of B_2O_3 may then be calculated.

PART III.

VOLUMETRIC ANALYSIS.

200. Introductory Remarks.—In the processes of volumetric analysis, volume is determined instead of weight. Volumetric methods are therefore applicable only to *fluids*, whose mobility enables them to adapt themselves to a measuring-vessel; the rigidity of solids renders it impossible to determine their volume directly and rapidly. The weight of a solid is therefore more easily determined than its volume.

Since both liquids and gases are dealt with volumetrically, volumetric analysis is divided into two sections, the one treating of liquids and the other of gases. The expression "Volumetric Analysis" is, however, generally applied to liquids only; the term "Gas Analysis" being usually applied to the estimation of gases.

Advantages of Volumetric Methods.—The chemical reactions, upon which analysis commonly depends, occur only when one at least of the reacting substances is in the liquid condition. Since liquids have, therefore, to be dealt with during the analysis, a great saving of time may usually be effected, by carrying on the processes in such a way that measurement of volume may, as far as possible, take the place of weighing.

This economy of time is effected by dissolving a known weight of a substance in a known volume of water. If a known fraction of this solution is then measured off, it will contain a corresponding fraction of the weight of the dis-

solved solid; and thus the necessity for further weighing is avoided. An additional advantage gained by this method of procedure is, that minute quantities of substance can be dealt with, which could not possibly be weighed. Hence it will be seen that volumetric methods will in certain cases surpass gravimetric methods in accuracy and in delicacy.

Illustration of a Volumetric Determination.—The estimation of chlorine present as chloride in a substance, by adding to its solution silver nitrate solution, will serve as an illustration of volumetric methods. The estimation depends upon the following reaction:—$NaCl + AgNO_3 = AgCl + NaNO_3$. The completion of this change is made evident by causing it to take place in the presence of potassium chromate solution. As soon as the silver nitrate is added in excess, it produces a permanent dark red precipitate of silver chromate; so that the appearance of a slight red coloration throughout the liquid indicates the completion of the reaction.

In a special estimation of chlorine present as chloride in a substance, the solution of silver nitrate contained one-tenth of the molecular weight of silver nitrate, or 16·994 grams, per litre. Hence, according to the above equation, each c.c. of the silver nitrate solution would precipitate 0·003545 gram of chlorine from the chloride. Of this silver nitrate solution 22·5 c.c. were required to exactly precipitate 2 grams of the substance dissolved in water. Therefore the weight of chlorine in the substance = 22·5 × 0·003545 = 0·07976 gram, and the percentage weight of chlorine in the substance = 0·07976 × 50 = 3·99.

Standard Solutions, Indicators, Reciprocity of the Process.—It will be seen from the preceding example that the solutions employed in volumetric analysis are required to be of known strength. Such solutions are commonly termed "*Standard Solutions.*"

It will also be noticed that some visible indication of the termination of the reaction is necessary

In certain cases this is furnished by a marked change in colour, as when potassium permanganate solution is added to warm acidified solution of oxalic acid: the colour of the permanganate is destroyed in this reaction, and a permanent pink tint in the liquid therefore indicates the presence of permanganate in excess, and proves that the reaction is completed.

In the majority of estimations, however, it is necessary to employ a third substance, which, by producing a change of colour, serves as an "Indicator" of the completion of the reaction. An illustration of this is furnished by the use of potassium chromate in the example already given.

The above process may evidently be utilised for the estimation of silver. For silver, when present in solution, may be estimated by adding its solution to standard sodium chloride solution in the presence of potassium chromate. This reciprocity is generally true of a volumetric process.

In the Following Description those processes of volumetric analysis are generally grouped together, in which the same liquid reagent or "Standard Solution" is employed. The most important and typical processes in each group are printed in ordinary type. Processes which are similar in principle to these, or are of less importance, are printed in smaller type. For additional methods of estimation, the student may consult *Sutton's Volumetric Analysis*, and *Fresenius' Quantitative Analysis.*

As a rule, each estimation which is made for practice in the method must be performed in duplicate, since the substances used are not generally of known and definite composition.

SECTION I.

MEASUREMENT OF LIQUIDS.
CALIBRATION AND USE OF GRADUATED VESSELS.
INDICATORS.
STANDARD SOLUTIONS.

The Measurement of a Liquid.

201. The Measurement of a Liquid may be undertaken for two different purposes.

(1). The volume of the whole liquid may be required. The liquid is then introduced into a suitably graduated measuring vessel.

(2). A known volume of the liquid may be required. It is then delivered from a suitably graduated measuring vessel in precisely the requisite quantity.

202. Graduated Glass Vessels are therefore adapted either to "measure" or to "deliver" a liquid.

Vessels of both classes are always marked with the temperature at which the liquid is to be measured in them. This temperature is usually 15°·5 C., which is equivalent to 60° F. Careful attention to this uniformity of temperature in a series of measurements in liquids is absolutely necessary when strict accuracy is required, since the volume of a liquid undergoes appreciable alteration by variations of temperature.

203. Absolute Volume.—It should be noted that some analysts employ measuring-vessels, which are graduated according to the absolute c.c. unit. The cubic centimetre unit employed in the measuring-vessels, hereafter described,

is slightly larger than the absolute cubic centimetre; since the absolute c.c. is the volume of 1 gram of water at 4° C., and the c.c. in the measuring-vessel represents the volume of 1 gram of water at 15°·5 C. But since the measuring-vessels are used for ascertaining the *relative* and not the *absolute* volumes of liquids, no error is introduced if the vessels correspond one with another in the value of their graduations.

A correction to absolute volume can be applied, if necessary, from the known expansion of water at different temperatures, which is given in the Appendix. Thus if a flask contains 250 grams of water at 15°·5, its capacity in absolute c.c.'s will be $250 \times 1{\cdot}00097 = 250{\cdot}2425$ c.c. Since the absolute c.c. is used in the measuring-vessels employed for gas analysis, the two classes of vessels do not agree in their measurements. The above correction can, however, be applied if necessary.

The temperature of 15°·5 has been selected because it is the average temperature of the air.

Any other temperature, which is convenient under special conditions, may be selected; but it must then be employed during the calibration and use of all the measuring-vessels. It is evident, however, that in order to calibrate in absolute c.c., the weight of water at the given temperature, which corresponds to absolute c.c., must be calculated.

204. Relation of Weight to Volume.—It should be remembered also that when these measuring-vessels are used for pure water at 15°·5, the number of c.c. they indicate will represent the weight of the water in grams. In the case of a liquid of specific gravity different from water, the number of c.c. read off must be multiplied by the specific gravity of the liquid, in order to obtain the weight of the liquid in grams.

205. Measuring and Delivering.—A horizontal line, etched upon the surface of the glass of the measuring-vessel, indicates its capacity to that particular level. In a vessel which is intended both to measure and to deliver liquids,

each capacity must be indicated by a separate mark. One of these serves to *measure* the volume of a liquid, and the other to *deliver* the same volume.

206. Reading the Volume.—The vertical section of the surface of a liquid in a tube is a curve or meniscus. It is usual to read the lowest point of the surface-meniscus in measuring the volume of a liquid.

Great care must be taken that the measuring-vessel is placed in a truly vertical position, while the volume of the liquid is being read.

207. Calibration of Measuring-Vessels.—The accuracy of each measuring-vessel should be carefully tested, or the vessel should be "calibrated," by weighing or measuring a definite amount of water in it at 15°·5. This calibration must be made in a room as nearly as possible at the temperature of 15°·5 C., and the process must be carried on rapidly and without interruption, in order to guard against alteration of volume and loss of water by evaporation.

If it is desired to calibrate the measuring-vessel in absolute c.c.'s, the weight of the requisite volume of water at 15°·5 to be introduced into the flask must be calculated. Thus for a 250 c.c. flask, the weight of water at 15°·5 to be introduced would be $250 \times 0{\cdot}999081 = 249{\cdot}77$ grams. The above factor is the density of water at 15°·5, as is shown in the Table in the Appendix.

Measuring-vessels are of various forms. Some of these are described below.

The Measuring-Flask.

Note.—A graduated measuring-cylinder (**219**) is a convenient form of measuring-vessel, which may often supplement or replace the measuring-flask.

208. Measuring-Flasks graduated for 1 litre (1000 c.c.), for $\frac{1}{2}$ litre (500 c.c), for $\frac{1}{4}$ litre (250 c.c.), for 200 c.c., and

for 100 c.c., will be found convenient for general use. The level, at which the upper surface of the liquid stands, must be in the neck of the flask (fig. 63); and the neck should be narrow to insure accurate readings.

Two marks are usually etched upon the neck of the flask —one for measuring, and the other for delivering the volume marked on the flask (**205**). When the flask is filled to the lower mark it contains the stated volume; and when it is filled to the upper mark, the stated volume can be poured out or delivered from the flask.

FIG. 63.

209. Calibration of the Measuring-Flask.—Before a measuring-flask is used, it is necessary to calibrate it, that is, to ascertain whether it holds or delivers exactly the volume which is marked upon it. The following methods serve for calibrating the measuring and delivering capacities respectively.

The processes are somewhat complicated, owing to the fact that the volume of air which is displaced by a large quantity of water, is considerably greater than that which is displaced by the weights which counterpoise it. Hence, it becomes necessary either to weigh by substitution (**12**), or to apply a correction to the weight (**13**). The method of weighing by substitution is adopted here, since it is more simple than that of applying the correction.

210. Calibration of a Flask for Measuring.—The flask is first thoroughly cleansed and dried. It is then placed upon one pan of a fairly sensitive large balance. Gram weights, equal in value to the number of c.c. which the flask should measure, are then placed beside the flask on the pan. Thus a quarter-litre flask would have 250 grams placed beside it.

The flask and weights are then exactly balanced by placing common shot or other suitable counterpoise upon the other pan.

The flask and weights are then removed, leaving the shot upon the scale-pan. The flask is placed upon a level surface, and distilled water at 15°·5 is poured into it, until the graduation-mark on the neck is exactly touched by the lowest point of the meniscus of the water-surface. The neck of the flask is then carefully dried, and the flask is replaced upon the empty pan of the balance. If the balance is now in exact equilibrium, the graduation of the flask is correct, and no further trouble need be taken.

If the balance is not in equilibrium, one of two courses may be adopted. Either the flask is regraduated correctly (**211**), or the requisite correction is applied each time the flask is used (**212**); the latter course is less convenient.

211. *A Correct Graduation* is obtained by adding water to or removing it from that in the flask, until equilibrium is obtained. The flask is then again placed upon a level surface, and a scratch is made on the neck with the point of a hard file on a level with the lowest point of the meniscus. This will give the true graduation for measuring.

212. *The Correction to be Applied to the Flask* is ascertained as follows. The flask is filled exactly to the mark and is placed upon the pan of the balance. Equilibrium is then secured by adding the requisite weights to one of the pans. The value of these weights in grams is taken as representing the same number of c.c.; and this volume must be added to the volume marked on the flask, if the weights have been placed upon the counterpoise pan; or the volume must be subtracted from that of the flask, if the weights have been placed on the same pan as the flask. This corrected capacity of the flask should be marked upon it.

213. Calibration of a Flask for Delivering.—The flask is filled with distilled water to the graduation on its neck. The water is then poured out, and the flask is allowed to drain in an inverted position for fifteen seconds. The flask, with its interior still wet, is now placed upon one pan of the balance,

after its neck has been closed by the stopper or by a rubber cork to prevent loss of weight by evaporation. On the same pan, weights are placed, whose value in grams is equal to the number of c.c. which the flask is marked to deliver. The flask and weights are then counterpoised by shot placed upon the other pan of the balance.

The flask and weights are then removed from the scale-pan; the flask is placed on a level surface, and is accurately filled to the delivering-mark. It is then replaced upon the pan together with the stopper. If the balance is now in equilibrium, the flask was correctly graduated. If equilibrium is not produced, correction must be applied (**211, 212**). This corrected volume will be delivered by the flask when it is accurately filled to the delivering-mark, and is allowed to drain for fifteen seconds after pouring out the liquid.

EXPERIMENT.—Calibrate a quarter-litre flask in the manner described above (**210–213**), so as to hold and to deliver 250 c.c. If the measuring-flasks of different capacities have not been already calibrated, they must be treated in the same way before they are used.

THE PIPETTE.

214. The Pipette is a tube which is intended either to deliver smaller fixed quantities of liquid than measuring-flasks do, or to deliver varying small volumes of liquid. The pipette for delivering a fixed volume is shown in fig. 65, and that for varying quantities in fig. 64.

The pipette is narrowed at each end. The liquid is introduced by applying suction from the mouth at the upper end, while the lower end is dipped into the requisite liquid. The liquid is thus raised to a higher level than the graduation. The upper end is then rapidly closed by pressure with the end of the first finger; and by carefully relaxing the pressure, the liquid is allowed to flow out below, until the lower curve of the meniscus just reaches the graduation required.

If the pipette has only one graduation, the measured volume may now be delivered into any vessel by removing

the finger, and then allowing the pipette to drain for fifteen seconds with its end touching the inside of the vessel.

If the pipette is graduated throughout its length, a certain fractional quantity of its entire contents may be delivered, by carefully relaxing the finger-pressure until the requisite quantity only has flowed out.

FIG. 65.

FIG. 64.

215. Calibration of the Pipette.—The process of calibrating, or testing the accuracy of a pipette, may be carried out as follows.

The clean and dry pipette is first provided with an arrangement for closing its delivering end, so that it may be weighed while it contains water.

This may be simply effected by stretching a strip of thin rubber sheet, about 4 inches in length and $\frac{1}{4}$ inch in width, over its lower end. An ordinary rubber ring of the proper dimensions, if cut across at one part, answers very well. The middle of the strip is pressed against the tip of the pipette so as to close it, and the strip is retained in position by drawing its free ends up on opposite sides of the pipette. The ends are then fastened down, while the strip is in a state of slight tension, by twisting a piece of copper binding-wire over them and round the pipette-tube. The band thus forms an elastic loop, which can be stretched over the tip of the pipette, and will effectually close it.

The rubber loop having been drawn aside, the pipette is filled up to the graduation with distilled water by suction, and its lower end is externally dried. The water is then allowed to flow out, and the pipette is permitted to drain for fifteen seconds in an erect position, with the tip touching the inside of the beaker. The pipette is now laid down in a horizontal position, and the rubber-loop is stretched over its tip. It is then laid upon the pan of the balance, and is accurately counterpoised without delay.

The pipette is then held in an upright position, and distilled water at 15°·5 is introduced from the fine jet of a wash-bottle into the top of the pipette, until the lowest point of the surface meniscus of the water just touches the graduation-mark. The water-level may be adjusted, if necessary, by means of a piece of glass tube drawn out into a long slender capillary. This is pushed down the pipette, and by its means water can be readily introduced, or sucked out, as may be necessary.

As soon as the pipette is exactly filled, it is once more laid upon the scale-pan. A weight in grams, equal in value to the number of c.c. the pipette should deliver, is now added to the counterpoise of the empty pipette. If this produces exact equilibrium, the pipette is correctly graduated.

If the balance is not in equilibrium, the quantity of water in the pipette is gradually increased or diminished by means of the drawn-out tube, until equilibrium is obtained. A file-mark is now made at the bottom of the water meniscus, and will furnish the correct graduation.

An alternative method, if the pipette is found to be incorrect, is to ascertain its true capacity (**212**), and to consider this as the volume which it delivers.

EXPERIMENT.—A 25 c.c. pipette may be calibrated as is described above. All the pipettes, which are to be used, must be similarly calibrated if they are not known to be correct.

THE BURETTE.

216. The Burette differs mainly from the graduated pipette by being open to atmospheric pressure at the top while it is in use. Further, the liquid is allowed to escape at the lower end by some contrivance by which a graduated outflow of the liquid can be permitted and immediately stopped when desired.

The burette is shown in fig. 66. It is a tube of equal diameter throughout its length. Its upper end is turned over at the edge. It is a great convenience to have the top of the burette widened and shaped into a small conical

funnel: this may be effected by softening the glass in the blowpipe-flame, and opening it out by means of a conical piece of charcoal. The lower end is considerably narrowed, and is closed either by a glass tap or by a pinch-cock pressing on a rubber joint.

FIG. 66.

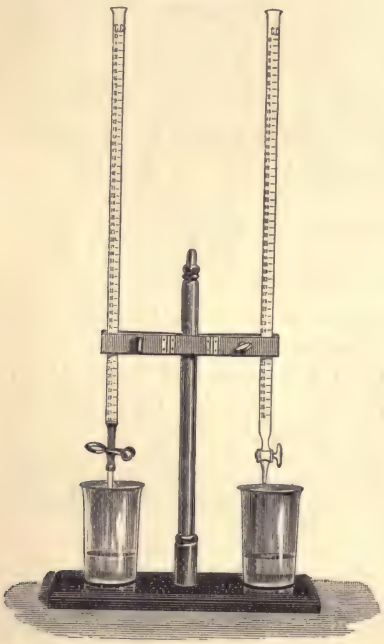


FIG. 67.

FIG. 68.

The burette is graduated throughout the greater part of its length into cubic centimetres and fractions thereof. Burettes are made to contain 20 c.c., 50 c.c., or 100 c.c. Those of 50 c.c. capacity are generally the most convenient.

The burette is usually filled by closing its lower end and pouring in liquid from the top. The liquid should rise above the highest graduation, and should then be allowed to escape from below until the lowest point of the meniscus just touches this graduation (fig. 67).

In filling the burette great care must be taken that no air-bubbles are left in the tap or jet. When the burette is in use, it is assumed that *liquid only* passes out. The volume of any air-bubble, which is swept through, would be counted as so much liquid, since the volume of liquid which has been taken out of the burette is measured by the fall of the liquid surface.

The burette is supported by being clamped in a convenient stand (fig. 66). It should not be held in the hand after it is filled, else error is introduced by the expansion of the liquid contents by heat.

To facilitate exact reading, Erdmann's float (fig. 68) is often used. It is somewhat smaller in diameter than the burette, and carries a horizontal mark on its surface. The float keeps uniformly immersed in the liquid, and sinks with it. The graduation on the burette, which corresponds with the mark on the float, is read off.

If the float is not employed, the meniscus curve of the liquid surface in the burette is easily seen, when a card is held in an inclined position behind the burette and near the surface of the liquid. The curve is then seen with a sharp black outline.

If the liquid in the burette is very dark in colour, the upper surface of the liquid is read off without using a float.

217. Calibration of the Burette.—The burette is charged with distilled water at 15°·5 C., and the tube below is carefully freed from air-bubbles. The calibration is then effected by allowing successive quantities of water, of 5 c.c. each, to flow into a tared stoppered flask or weighing-bottle. The weight in grams of the water thus run off should be exactly equal to the volume of the water in c.c. as indicated by the burette.

218. If the reading of the burette is found to be inaccurate, a table should be drawn up showing its true capacity up to each graduation: the error between two successive weighings being distributed equally between the graduations included in the 5 c.c.

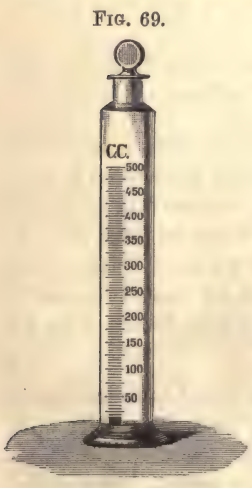
Thus in calibrating from 0 to 10 c.c. on a burette, the following weights of water were obtained. From 0 to 5, 4·9549 grams; and from 5 to 10, 4·9781 grams. The first c.c. division on the burette therefore corresponds to $\frac{4·9549}{5}$ = 0·99098 c.c.; the second division corresponds to 0·99098 × 2 = 1·98196 c.c., and so on for the first five divisions. Similarly the sixth division will contain $\frac{4·9781}{5}$ = 0·99562 c.c. Therefore the first six divisions of the burette will contain 4·9549 + 0·99562 = 5·95052 c.c.; and seven divisions will contain 5·95052 + 0·99562 = 6·94614 c.c.

EXPERIMENT.—A 50 c.c. burette may be calibrated in the above manner; but all burettes must be similarly tested before being used.

THE MEASURING-CYLINDER.

219. Measuring Cylinders of thick glass are useful to supplement, or replace, the measuring-flasks. But since the surface of the liquid in the cylinder is greater than in the flask, the accuracy of the reading is diminished in the cylinder.

FIG. 69.



The cylinder is usually graduated throughout the greater part of its length; the successive graduations indicating from 1 to 10 c.c. each, according to the dimensions of the cylinder. As in the case of the flask, the cylinder may be graduated either to *measure* or to *deliver* the liquid.

Measuring-cylinders are of two kinds. One kind is narrowed at the top, and can be closed by a clean rubber cork or by an accurately ground stopper (fig.

69). This form is convenient for shaking and mixing the liquid contents without risk of loss. The other kind of cylinder is open at the top, and is furnished with a lip for pouring out.

220. Calibration of the Measuring-Cylinder.—A cylinder for measuring is most rapidly calibrated by allowing water to flow into it from a previously calibrated burette, and thus ascertaining whether the graduations of the cylinder are correct. If they are not correct, it will be necessary to construct a table, in which the true value of each graduation is shown, as is described above in the case of the burette (218).

EXPERIMENT.—A quarter-litre cylinder should be calibrated as is directed above, adding 10 c.c. from the burette each time. All other measuring-cylinders must be calibrated in this way before they are used.

AGREEMENT OF MEASURING-VESSELS WITH ONE ANOTHER.

221. It is necessary to ascertain that all the different measuring-vessels agree one with another in the value of their graduations.

For most purposes of volumetric analysis, it is not necessary that each vessel should be absolutely accurate, when it is tested by weighing distilled water in it at a standard temperature. It is sufficient that the relative value of the measurements given by the different vessels should correspond. But this relative correspondence is absolutely necessary.

Thus two quarter-litres when delivered into the half-litre measuring-flask must fill it to its graduation; the 50 c.c. pipette, when its contents are emptied five times in succession into the quarter-litre measuring-flask, must exactly fill it to its graduation.

Evidently a strictly accurate system of correction, applied to all the vessels by water-calibration, will insure this relative

accuracy. By proceeding as is suggested above, the correctness of the previous calibration can be ascertained.

Indicators used in the Volumetric Estimation of Acids and of Alkalis.

The indicators, mentioned below, serve to show the approach, and finally the exact attainment, of the point of neutralisation when an acid and alkali are mixed. Other indicators which are required for special purposes will be described hereafter.

222. General Caution in using Indicators.—It should be remembered that when the end of a reaction is judged by means of an indicator, or by means of any final colour-change, it is necessary that the one liquid should be added to the other in all cases in the same order, else the results will not exactly correspond.

Thus, if litmus is used as an indicator in titrating an acid by adding the acid to standard caustic alkali solution, in all processes of estimating acid by the alkali in the presence of litmus, the acid should be run into the alkali and not the alkali into the acid.

223. Litmus Solution.—This solution is used both for acids and for alkalis. The solution is most sensitive when it is of a purple colour. The presence of an excess of acid causes the litmus to assume a bright red tint: excess of alkali produces a pure blue tint. The solution may be prepared as follows.

Digest about 10 grams of solid litmus with about 250 c.c. of distilled water for a few hours in a warm place. Decant the clear liquid from the residue, and add dilute nitric acid in sufficient quantity to change the colour of the solution to distinct purple.

A More Sensitive Litmus Solution may be made as follows. Extract all the colouring-matter from the solid litmus, by repeatedly

digesting it with hot water. Evaporate this solution to a moderate bulk, and add a slight excess of acetic acid so as to convert all carbonates present into acetates. Again evaporate the solution over a water-bath until it becomes pasty, and then add an excess of methylated spirit. The spirit will precipitate the blue colouring-matter, while a red colouring-matter, together with the alkaline acetates, will remain in solution. The precipitate is transferred to a filter, and is washed with spirit. The pure colouring-matter is then dissolved in warm water: and the solution is rendered purple by the cautious addition of dilute nitric acid.

This solution should be kept in a corked bottle: and the cork should be deeply grooved, so as to allow free access of air to the contents of the bottle. Even when this precaution is taken, the colour of the liquid gradually fades; it may usually be restored, however, by exposing the solution to the air in an open dish.

Small quantities of this solution may be conveniently transferred to the solutions which are to be titrated, by means of a small pipette, made by drawing out a piece of glass tube at one end. The pipette is fitted into a perforation in the cork, which is in the neck of the store-bottle.

When some litmus solution is to be removed, the narrow end of the pipette is immersed in the liquid, and the upper end is closed by the finger. By this means the requisite quantity of liquid can be taken out. If definite quantities of the solution are to be used, file marks may be made on the tube to denote the volumes. Marks made for delivering 2 c.c., 1 c.c., and 0·5 c.c. will be found generally convenient.

The presence of free carbonic acid interferes with the blue colour of litmus. Accordingly in titrating an acid solution by running it into an alkaline carbonate, the litmus solution turns from blue to purple before the point of neutralisation by the acid is arrived at. This is due to the liberated carbonic acid acting upon the litmus. The carbonic acid can be removed by boiling the liquid; and the point of neutrality is known to have been just passed, and the reaction is therefore complete, when the solution has assumed a bright red colour which does not change when the liquid is boiled.

224. Litmus Paper.—A moderately strong solution of purple neutral litmus solution is prepared, and strips of glazed paper are drawn through it. The strips are hung up to dry in a room free from acid fumes. Ordinary glazed paper produces a more sensitive test paper than filter-paper does.

225. Cochineal Solution.—This indicator is not affected in colour by carbonic acid. It also possesses the advantage, that its change of colour can be more readily seen by gas-light than is the case with litmus.

The solution is prepared by digesting about 10 grams of powdered cochineal for several hours at a gentle heat in a litre of weak spirit, made by mixing 200 c.c. of methylated spirit with 800 c.c. of water. The clear liquid is decanted from the sediment, and is ready for use.

The colour of the solution is yellow; and this is turned to reddish-violet by alkalis. This reddish-violet solution of cochineal is changed to yellow again by mineral acids, but is not as easily affected by weak organic acids. The solution should not be used in the presence of compounds of iron or of aluminium, or of acetates.

226. Turmeric Paper.—Turmeric paper is mainly used in volumetric analysis in the process for the estimation of CO_2 in air by Pettenkofer's method. The yellow colour of the paper is changed to reddish-brown by alkalis. Since turmeric is gradually bleached by exposure to daylight, the test-paper should be kept in the dark.

The paper is prepared as follows. Powdered turmeric-root is digested two or three times with small quantities of water. This treatment removes some objectionable inert colouring-matter. The active colouring-matter is then extracted by digesting the powder with methylated spirit, which has been diluted with twice its volume of water. Strips of filter-paper are drawn through the clear solution thus obtained, and are hung up to dry in the air with as little exposure to daylight as possible.

227. Methyl Orange. This substance is also known as

Tropaeolin D, or Orange III.—This indicator is not affected by carbonic acid. In alkaline solution its colour is yellow, but this colour changes to red on the addition of an acid. The solution does not decompose or undergo change by being kept.

The solution is prepared by dissolving 1 gram of methyl-orange in a small quantity of methylated spirit, and making the solution up to 1 litre with methylated spirit diluted with its own volume of water.

228. Phenol Phthalein.—The alcoholic solution of this indicator is colourless. When a few drops are added to the solution of an alkali, the liquid assumes an intense red colour: this colour is readily destroyed by both mineral and organic acids. Phenolphthalein cannot be used in the presence of carbonic acid, or of ammonium salts; it is therefore not suitable for estimating ammonia.

Standard Solutions.

229. Standard Solutions.—The solutions of definite strength which are used in volumetric analysis are termed *Standard Solutions.* A standard solution may be made of any strength, which is suitable for the particular estimation to which it is applied.

230. Normal Solution.—A standard solution is said to be of *Normal, or Equivalent Strength,* when 1 litre contains the equivalent weight in grams of an element, acid, alkali, or salt.

By the term equivalent is understood the weight in grams of the substance which is chemically equivalent to 1 gram of hydrogen, to 40 grams of sodium-hydrate, to 36·5 grams of HCl, or to 53 grams of Na_2CO_3.

Thus a normal solution of KOH will contain 56·1 grams of the solid substance, and a normal solution of HNO_3 will contain

63 grams of the acid. But the normal solution of Na_2CO_3 will contain only $\frac{106{\cdot}12}{2} = 53{\cdot}06$ grams of that salt per litre, since the molecule of monobasic hydrochloric acid can neutralise only half a molecule of sodium carbonate. Similarly, the *normal* solution of dibasic sulphuric acid will contain only $\frac{98}{2} = 49$ grams per litre.

A solution of one-half the normal strength is a *Semi-normal Solution* $\left(\frac{N}{2}\right)$; if it is of one-tenth the normal strength it is *Deci-normal* $\left(\frac{N}{10}\right)$; and if it is of one-hundredth the normal strength, it is *Centinormal* $\left(\frac{N}{100}\right)$.

231. Molecular Solution.—A standard solution which contains the molecular weight of the substance in grams in 1 litre, may be distinguished as a *Molecular Solution*. Solutions of fractional strength being distinguished by the prefixes semi-, deci-, and centi- respectively. These are shortly denoted by $\frac{M}{2}$, $\frac{M}{10}$, and $\frac{M}{100}$.

232. Storage and Preservation of Standard Solutions.—A Winchester quart-bottle is suitable for the storage of large quantities of solution. The bottle which is to contain the solution should not only be clean but dry. If it has been recently washed and is still wet inside, it must be rinsed out with a portion of the standard solution, since the introduction of water would alter the strength of the standard solution. As soon as the solution has been introduced the bottle should be at once securely stoppered, and labelled with the name, strength, and date of the preparation of the solution; the label should also bear the initials of the maker of the solution.

Evaporation of water from the standard solution invariably occurs when the bottle is opened for use, and even takes

place slowly while the bottle is closed. In some solutions the substance in solution itself undergoes change in course of time. Hence a standard solution usually alters in strength when it is stored, and the amount of this alteration will depend upon the extent of its use, and upon the length of time it has been stored. It is, therefore, important to be able to judge, by noting the date of its preparation, the probable risk of serious change in the strength of the solution.

It must further be remembered that, unless the bottle is completely filled with the solution, internal evaporation and condensation will lead to the formation of drops of pure water on the upper part of the interior of the bottle. Care must, therefore, be taken to shake the bottle before removing the stopper, so as to mingle this water once more with the solution.

Standard solutions should be kept in a cool place, since the evaporation of water from the solution will naturally be less, as the temperature of the store-room is lower.

Loss by evaporation is checked by drawing a tightly-fitting rubber cap or finger-stall down over the stopper and neck of the bottle. This also serves to keep the lip of the bottle clean. Another method of preventing evaporation is to close the bottle with a rubber stopper instead of with an ordinary cork. If a glass stopper is used, it should be somewhat too small for the neck of the bottle; the ground part of the stopper is then surrounded with a suitable piece of black rubber tubing. When the stopper is thus prepared, it must fit into the neck of the bottle tightly. Rubber stoppers are always to be preferred for bottles containing solutions of caustic alkali, since a glass stopper becomes set fast by the action of the alkali.

Some standard solutions undergo change by the action of light, and should be kept in a dark place.

SECTION II.

ALKALIMETRY AND ACIDIMETRY.

The student should note that many directions and precautions, which are of general importance in the preparation of standard solutions, are given in paragraphs 233–239. These are not repeated under subsequent preparations.

Normal Sodium Carbonate Solution.

233. This solution is prepared by dissolving pure Na_2CO_3 in distilled water in the proportion of 53·06 grams per litre. It is therefore a semi-molecular solution.

When sodium carbonate is dissolved in water, it causes contraction of volume to occur: a similar contraction occurs in the preparation of many other solutions. Hence an accurate result is not obtained by dissolving the requisite weight of the salt in the measured volume of water. The solution must be made up to its true volume at the proper temperature in the measuring-vessel itself, and with constant mixing.

Pure Na_2CO_3 is most readily obtained by igniting sodium bicarbonate.

The bicarbonate should first be tested for traces of chloride and sulphate. This is effected by shaking it for some time in a stoppered bottle with a small quantity of distilled water, and then applying the necessary tests to the clear liquid. If chloride or sulphate is present, the bicarbonate is purified by shaking about 100 grams with a small quantity of distilled water, allowing the salt to settle, and decanting the liquid.

The washing is repeated with fresh portions of distilled water, until the last washing-water gives no reaction for sulphate or for chloride; the bicarbonate is then drained on a porous tile and is dried by pressing it between dry sheets of filter- paper.

A quarter of a litre of the normal solution of Na_2CO_3 will suffice for present purposes. This is prepared as follows.

About 23 grams of the pure bicarbonate are spread in a thin layer inside a weighed platinum or porcelain dish. The dish and its contents are then heated over a Bunsen-flame to dull redness for about twenty minutes, care being taken not to fuse the salt. After it has cooled in a desiccator, the dish is weighed. It is then heated again for ten minutes, allowed to cool, and weighed. These processes are repeated until the weight remains constant. The weight of pure Na_2CO_3 in the dish is now found by subtracting the weight of the dish. The standard solution may be prepared from this carbonate by **233** or by **234**, and is at once stored in an accurately-stoppered bottle.

234. The Volume of the Normal Solution, which would contain the above weight of Na_2CO_3, is found by Calculation.—Thus if the sodium carbonate weighed 13·5 grams, it will furnish $\frac{13{\cdot}5 \times 250}{13{\cdot}265} = 254{\cdot}4$ c.c. of the normal solution, since 13·265 grams of Na_2CO_3 are required for 250 c.c. of normal solution. The procedure is as follows.

The weighed carbonate is transferred from the dish to a beaker, without loss; and the dish is rinsed out into the beaker with successive small quantities of distilled water, until every trace of the carbonate has been removed.

The carbonate is then dissolved in the beaker by stirring, the solution is poured down the stirring-rod into the 250 c.c. flask or cylinder, and the beaker is rinsed with three or four successive small quantities of water, which are also poured down the rod into the flask. The liquid is made nearly up to the 250 c.c. mark with distilled water at 15°·5, and is constantly mixed by shaking. The neck of the vessel is then

closed by a stopper or by a clean dry rubber cork, and its contents are thoroughly mixed by shaking.

The solution is finally made up precisely to the mark by placing the vessel on a level surface, and slowly filling in water from a pipette, or burette, or from a wash-bottle with a fine jet. The bottom of the meniscus of the liquid surface must now just touch the graduation. The volume of water required to make the liquid up to 254·4 c.c., which in the above example amounts to 4·4 c.c., is then added from a burette. The liquid is then once more thoroughly mixed. This may be effected by inverting and rotating the vessel, so as to make the movement of the inclosed air thoroughly mix together all parts of the liquid.

235. The Weight of Sodium Carbonate is brought to exactly 13·265 grams, and this is dissolved to a quarter-litre. The adjustment of the weight may be effected by removing small quantities of the carbonate from the dish with the point of a pen-knife, while the dish is on the scale-pan, the weights having been first adjusted on the other pan so as to be equal to the weight of the dish + 13·265. The salt is then dissolved in a beaker as is described above (**234**), and the solution will be normal, when the flask is filled exactly to the graduation, and the liquid is well mixed.

Normal Sulphuric Acid.

236. This solution is a semi-molecular one, and should therefore contain 49·03 grams of pure H_2SO_4 per litre.

It is prepared as follows. An appropriate quantity of pure strong oil of vitriol is diluted with water in a thin glass vessel. The hot mixture is then cooled, and its strength is ascertained by titrating a portion of it with normal sodium carbonate solution (**233**). As soon as the strength of this diluted acid is accurately known, the amount of further dilution with water, which is necessary to reduce it to the normal condition, may be easily calculated.

Measure out 30 c.c. of pure oil of vitriol, and allow this to flow into about 200 c.c. of distilled water contained in a

thin glass flask. Mix the liquids well, and cool the mixture by shaking it round in the flask, while a stream of tap-water flows over its exterior. Now make the liquid in the flask up to one litre, mix it thoroughly, and titrate a portion of it with the sodium carbonate solution as is described below.

A clean and well-drained 20 c.c. pipette is partly filled with the normal sodium carbonate solution by suction: the liquid is shaken round in the pipette, and is allowed to flow away into the sink. The pipette is then once more charged with the normal solution exactly to the 20 c.c. mark, by sucking up more than the requisite volume, quickly applying the first finger to the top of the pipette, and slowly allowing the excess to flow out. The 20 c.c. of liquid is then delivered into an 8-oz. beaker, and water is added.

If the interior of the pipette was not only clean but perfectly dry, the preliminary rinsing with the solution may be neglected, since in that case there is no danger of diluting the standard solution with water adhering to the interior of the pipette.

A burette has now to be charged with the diluted acid. If the interior of the burette is not perfectly dry, it must be rinsed with a small part of the acid; this liquid is rejected. The burette is then filled with the acid, and air-bubbles are carefully removed from the tap or jet below, by allowing some of the liquid to flow rapidly through into the bottle. The burette is then finally filled precisely to the zero mark.

A few drops of methyl-orange solution (**227**) are now added to the sodium carbonate solution in the flask to serve as an *indicator*. This serves to indicate when the sodium carbonate has been exactly neutralised by the addition of the dilute acid from the burette.

The flask is now placed upon a white plate or tile, and the acid from the burette is dropped gradually into the sodium carbonate solution, and is constantly mixed with the solution by shaking. The addition of acid is continued, until the yellow colour of the liquid just begins to change to red.

It is important that the acid should be added in the slightest possible excess. The change to permanent red

must therefore be produced only by the addition of the last drop of acid.

If Neutral Litmus Solution (223) is used as the indicator in this titration, it must be remembered that the change of colour to red does not indicate complete neutralisation by the conversion of the alkaline Na_2CO_3 into neutral Na_2SO_4, because the CO_2, which is liberated in the reaction, dissolves in the cold liquid and exerts an acid reaction upon the litmus.

In order to expel this dissolved CO_2, the liquid in the flask is boiled for a few minutes, and the blue colour, which is thus restored, is again just converted into bright red by the cautious addition of acid from the burette.

The liquid is now once more boiled, and if the red colour of the litmus remains unchanged, the neutralisation is complete. If the colour still changes on boiling, the above processes must be repeated until the liquid remains bright red after it has been boiled for a few minutes.

A comparison-flask may be prepared, in which a similar quantity of water and litmus solution has been made distinctly red by addition of acid. This will serve to show the bright red tint which must be obtained in the test-flask.

The volume of the dilute acid solution which has been required for the neutralisation of the sodium carbonate in the flask is now read off on the burette; and this result is confirmed by a repetition of the "titration" in a precisely similar manner with a fresh quantity of the sodium carbonate solution. The two titrations should not differ by more than 0·1 c.c.

237. These titrations will prove that the acid solution is somewhat too strong. It may be made normal by proceeding as is described in the following example.

The 20 c.c. of the alkaline solution were exactly neutralised in a special case by 18·4 c.c. of the acid solution. It follows that 18·4 c.c. of the acid will require to be diluted to 20 c.c. in order to furnish a standard acid, which is exactly equivalent to the alkaline solution. A litre of normal acid is therefore made by measuring $18{\cdot}4 \times 50 = 920$ c.c. of the acid into a litre flask, and then diluting this to 1 litre with distilled water. This diluted acid is now thoroughly mixed, and is once more

titrated with the alkaline solution, as has been already described (**236**), in order to prove its correctness.

238. Correction of Standard Solutions by means of Factors.—A standard solution usually becomes more or less altered in strength after it has been stored for some time (**232**). The standard acid will therefore require to be occasionally examined by titrating it against a freshly-prepared sodium carbonate solution.

It will be found generally convenient to use about 20 c.c. of a solution for ascertaining its strength by titration. The titration is usually effected from a 50 c.c. burette, and this should furnish enough liquid for two titrations.

It is not usual to bring back a solution, which is found to be slightly in error, to its true standard. Instead of this a correction is applied to the solution when it is used. The method of correcting the solution will be rendered intelligible by the following example.

In a special case 19·8 c.c. of the standard acid solution were required instead of 20 c.c. to neutralise 20 c.c. of the freshly-prepared normal sodium carbonate solution. Accordingly the number of c.c. of this acid which have been employed in any titration will require to be multiplied by $\frac{20}{19{\cdot}8} = 1{\cdot}01$, in order to find the number of c.c. which would have been required if the acid had been normal. The number 1·01 is termed the "Factor" of the solution.

"The Factor," which is required for the correction of a standard solution, should be entered upon the label of the bottle from time to time, with the date of its determination.

Normal Sodium Hydrate Solution.

239. A solution of sodium hydrate, which is free from sodium carbonate and from other sodium compounds, may be prepared by the action of metallic sodium upon distilled

water. Sodium hydrate, which has been purified by solution in alcohol, may be purchased, but this furnishes a less pure solution.

The solution is prepared from metallic sodium by weighing about 25 grams of clean sodium. The metal is cut into small pieces, and these are introduced, one by one, into recently boiled and cooled distilled water contained in a platinum or silver dish. The dish is covered with a clock-glass immediately after the addition of each piece of metal, in order to prevent loss of NaOH by spirting; and the reaction is allowed to complete itself, before each successive addition of the metal.

If sodium hydrate, purified by alcohol, is used, about 44 grams are weighed and dissolved in water.

In either case the solution of the hydrate is diluted to a litre with distilled water, which has been recently boiled and cooled so as to insure its freedom from carbonic acid. 20 c.c. of the solution are then mixed with a few drops of methyl-orange (**227**) to serve as an indicator, and are titrated with normal sulphuric acid (**236**) from a burette. The sodium hydrate solution is then brought to the normal strength by diluting it to the requisite extent with distilled water (**237**).

This solution should be restandardised occasionally, since it is subject to change. The bottle, which contains it, should be closed by a rubber stopper (**232**), since a glass stopper is apt to become set fast.

Normal Hydrochloric Acid.

240. Pure strong hydrochloric acid has a specific gravity of 1·14, and contains 28 per cent of HCl. About 150 c.c. of this acid are diluted to a litre. The exact strength of this solution is then ascertained by titration with normal sodium hydrate solution (**236**). The acid solution is then brought to standard strength by dilution (**237**).

Estimation of the Total Acid in Vinegar.

241. The estimation depends upon finding the amount of semi-normal sodium hydrate solution, which is required to neutralise the acid present in a known quantity of the vinegar.

25 c.c. of the semi-normal sodium hydrate solution (**239**) are measured by a pipette into a small flask. The vinegar is then added to the alkaline solution from a burette with constant mixing, until a drop of the liquid just reddens blue litmus-paper when it is placed upon the paper by a thin glass rod. This indicates the end of the titration.

If the vinegar is colourless or nearly so, a few drops of neutral litmus solution may be added to the liquid in the flask instead of using litmus-paper, and this renders the process of titration more rapid.

The point of neutrality is still more rapidly ascertained by adding a little phenol-phthalein solution instead of litmus to the sodium hydrate solution in the flask. The vinegar is added from the burette until the red colour disappears. This indicator may be used even with coloured vinegar.

In calculating the percentage weight of pure acetic acid which is present in the vinegar, it should be noted that according to the equation $C_2H_4O_2 + NaOH = NaC_2H_3O_2 + H_2O$, 60·01 grams of acetic acid exactly neutralise 40·06 grams of NaOH.

Therefore each c.c. of the semi-normal sodium hydrate solution will neutralise $\frac{60{\cdot}01}{2 \times 1000} = 0{\cdot}03$ gram of acetic acid. The amount of vinegar, which is required to neutralise the 25 c.c. of sodium hydrate, will accordingly contain $25 \times 0{\cdot}03 = 0{\cdot}75$ gram of acetic acid. The number of c.c. of vinegar measured out may now be taken as the weight of the vinegar in grams (**242**); and the percentage weight of acetic acid in the vinegar is then calculated by proportion.

242. The Weight Burette.—For ordinary purposes it is sufficiently accurate to assume in the above calculation that each c.c. of vinegar weighs 1 gram. This is, however, only absolutely true of pure water. And since the specific gravity of vinegar differs slightly from that of water, the number of c.c. of the vinegar should be multiplied by its specific gravity (**23–28**), in order to obtain its true weight.

The correction thus applied necessitates the determination of the specific gravity of the vinegar. This may be avoided if the ordinary measuring-burette is replaced by a weight-burette (fig. 70). The weight-burette is a small, thin flask with a narrow delivery jet, and a broader opening to be closed by the finger. The clean and dry burette is half filled with vinegar and weighed.

FIG. 70.

The vinegar is then gradually added to the sodium carbonate solution precisely as is directed above (**241**). The burette with the remaining vinegar is again weighed, after the titration has been finished. The *weight* of vinegar used in the titration is equal to the difference between the two weighings.

The burette must be kept stoppered when it is not in use, in order to guard against loss of weight by evaporation.

INDIRECT ESTIMATION OF BARIUM OR CALCIUM IN SOLUTION BY STANDARD Na_2CO_3 AND ACID SOLUTIONS.

243. The method consists in adding a known volume of deci-normal sodium carbonate solution (**230, 233**) to the neutral solution containing the barium. The sodium carbonate must be present in quantity more than sufficient to precipitate the whole of the barium as carbonate. After the liquids have been thoroughly mixed by stirring, the barium carbonate is removed by filtration and is washed. The excess of sodium carbonate is then determined in the mixed filtrate and washings by titration with deci-normal hydrochloric acid solution (**230, 240**).

The results which are thus obtained furnish the weight of Na_2CO_3, which is necessary to exactly precipitate the barium as carbonate, and from this the weight of barium originally present in the solution can be calculated.

The following example will serve to illustrate the method of calculation. The barium solution was precipitated by adding to it 30·2 c.c. of deci-normal sodium carbonate solution. The excess of sodium carbonate required 5·4 c.c. of deci-normal hydrochloric acid for its neutralisation. Hence the volume of sodium carbonate solution required to precipitate the barium was $30·2 - 5·4 = 24·8$ c.c. Each c.c. of this solution contains 0·005306 gram of Na_2CO_3.

Now from the equation $BaCl_2 + Na_2CO_3 = BaCO_3 + 2NaCl$ it will be seen that 137 of Ba are precipitated by 106·12 of Na_2CO_3.

Therefore each c.c. of the Na_2CO_3 solution corresponds to $\frac{106·12 \times 0·005306}{137} = 0·00685$ gram of Ba.

Hence the weight of Ba present in the above solution $= 24·8 \times 0·00685 = 0·169$ gram.

244. A Less Rapid and Less Accurate Method consists in precipitating the barium as carbonate from a known quantity of its neutral solution, by the addition of sodium carbonate solution in excess. The filtered and well-washed precipitate is dissolved in a known volume of deci-normal hydrochloric acid (**44**), which must be added in slight excess; the solution is boiled for five minutes, and the excess of acid in the solution is then titrated by adding standard NaOH solution from a burette in the presence of methyl-orange (**227**).

The results thus obtained furnish the data for finding the weight of HCl which is required to convert the Ba from carbonate into chloride:—$BaCO_3 + 2HCl = BaCl_2 + CO_2 + H_2O$. From this the weight of Ba may be calculated.

Indirect Estimation of Ammonium in Solution by means of Standard Sodium Hydrate and Acid Solutions.

A method for estimating ammonia directly has been given in paragraph **138**. The indirect method described below is suitable to any ammonium salt of definite composition; this excludes the carbonate.

245. This method of indirect estimation of ammonia and of ammonium depends upon decomposing the ammonium compound by boiling it with excess of standard sodium hydrate solution (**239**), the boiling being continued until no more NH_3 escapes with the steam. The excess of sodium hydrate in the liquid is then estimated by titration with a standard acid, using litmus as an indicator.

As soon as the ammonia has been completely driven off by boiling the liquid, strips of moistened turmeric-paper, when held in the escaping steam, will no longer be rendered brown.

In the reaction which occurs, the quantity of sodium hydrate which is neutralised is proportional to the amount of ammonia which is evolved. Thus the following equation represents the reaction in the case of ammonium chloride :—

$$NH_4Cl + NaHO = NH_3 + NaCl + H_2O .$$

From this it is seen that 17·049 grams of NH_3 correspond to 40·063 grams of NaOH neutralised.

The Following Example will serve as an illustration of the process and of the calculation.

1·1302 grams of an ammonium salt were mixed with 25 c.c. of normal sodium hydrate solution, and the liquid was boiled until turmeric-paper was no longer discoloured, when it was held in the escaping steam. The liquid was then coloured by the addition of a few drops of litmus solution, and normal or semi-molecular sulphuric acid was added, until the litmus just turned bright red. The volume of acid required was 5 c.c.

Now, since the sodium hydrate and acid solutions are equivalent to one another, the amount of sodium hydrate solution which has been neutralised by the ammonium salt is $25 - 5 = 20$ c.c. And since each c.c. of the NaOH solution is equivalent to 0·017049 gram of NH_3, the weight of NH_3 present $= 20 \times 0{\cdot}017049 = 0{\cdot}3409$ gram.

Therefore the percentage of NH_3 present $= \dfrac{0{\cdot}3409 \times 100}{1{\cdot}1302} = 30{\cdot}16.$

And the percentage of NH_4 present $= \dfrac{18{\cdot}052 \times 30{\cdot}16}{17{\cdot}049} = 31{\cdot}91.$

SECTION III.

PROCESSES OF OXIDATION AND REDUCTION.

Estimation of the Available Chlorine in Bleaching-Powder by means of Alkaline Arsenite.

250. The composition of dry bleaching-powder, when it is in the freshly-prepared state, and fully charged with chlorine, may be represented by the formula $2CaOCl_2.Ca(OH)_2$. When this substance is treated with water, it yields a liquid which probably contains $CaCl_2$ and $Ca(OCl)_2$, together with some $Ca(OH)_2$. The value of the bleaching-powder depends on the amount of $Ca(OCl)_2$ which can be thus produced.

In the ordinary applications of bleaching-powder there is little doubt that the nascent oxygen furnished by the hypochlorite is the active agent. But it is not customary to estimate the value of bleaching-powder from the percentage of the hypochlorite, or of the nascent oxygen which it can furnish. The weight of chlorine, which is chemically equivalent to this oxygen, is ordinarily returned, and this is termed the "available chlorine."

When bleaching-powder of the above composition is acted upon by an acid, the *whole* of the available chlorine is given off, thus:—

$$2CaOCl_2.Ca(OH)_2 + 3H_2SO_4 = 2Cl_2 + 3CaSO_4 + 4H_2O.$$

Hence the weight of available chlorine in good bleaching-powder corresponds to the whole of the chlorine which it contains. The chlorine compounds which are present in the bleaching-powder may, however, be in a form which renders

them unavailable for purposes of chlorination or oxidation. This may arise from careless preparation or storage of the powder. Hence the available chlorine is not always equal to the total weight of chlorine present.

The formula already given represents bleaching-powder which contains about 40 per cent. of chlorine. But bleaching-powder does not commonly contain more than 35 per cent. of available chlorine, and the percentage sometimes falls as low as 20.

The amount of nascent oxygen, which bleaching-powder can yield, or its equivalent of "available chlorine," may be estimated in several ways. Two methods are described in paragraphs **251, 293.**

251. Estimation of the Available Chlorine in Bleaching-powder by the Oxidation of an Alkaline Arsenite.—When solution of bleaching-powder is brought into contact with an alkaline arsenite, the relative amounts of arsenious oxide and of oxidising agent which act upon one another are shown by the following equation:—

$$As_2O_3 + Ca(OCl)_2 = As_2O_5 + CaCl_2.$$

Here As_2O_3 is oxidised by O_2, and this O_2 is chemically equivalent to Cl_4. Hence the amount of oxidation is a measure of the "available chlorine." On this reaction the following process of estimation depends.

The Standard Solution of Arsenious Oxide.—The most convenient weight of As_2O_3 for this solution is the molecular weight divided by 40. This gives a deci-normal solution, since As_2O_3 corresponds to Cl_4 in the process of titration.

Accordingly the solution is prepared by weighing out accurately $\frac{198}{40} = 4{\cdot}95$ grams of pure resublimed arsenious oxide (**83,** Exp. 28) into an 18-oz. flask, and adding about 25 grams of pure sodium carbonate crystals. The flask is then half filled with water, and is heated on the water-bath until the arsenious oxide is dissolved. The solution is cooled

under the water-tap, by placing a small inverted beaker over the neck of the flask, and then allowing a gentle stream of cold water to run upon the beaker and thence over the surface of the flask.

As soon as the liquid is cooled down to 15°·5 C., it is transferred to a litre-flask, and the solution is made up to 1 litre with water at 15°·5. Each c.c. of the solution will contain $\frac{198}{40 \times 1000} = 0{\cdot}00495$ gram of As_2O_3, and this corresponds to 0·003545 gram of Cl. After the contents of the flask have been well shaken, they are transferred to a clean dry bottle, which is at once labelled with the name and strength of the solution, and the date of its preparation.

Preparation of the Bleaching-powder Liquid.—Weigh out on an *open* balance 10 grams of the bleaching-powder. Place the powder in a smooth porcelain mortar, preferably one which is glazed inside, and add a few c.c. of water. Rub the mixture into a paste by means of the pestle; then add more water and continue the rubbing until a thin cream is formed. Allow the solid to subside and decant the supernatant liquid into a litre-flask.

Then treat the residue repeatedly with fresh quantities of water, stirring up and pouring off after each addition, until the whole of the solid has been transferred to the flask. Finally, fill up the flask to the mark with water, and mix its contents well by shaking. The solution must be at once quickly titrated, since it undergoes rapid change. The liquid will always be milky, because bleaching-powder is not completely soluble in water.

Iodised Starch-paper is then prepared as follows. Shake up one part of pure starch with about a hundred parts of distilled water, and heat the mixture to boiling. Then add about one part of pure potassium iodide, and pour off the clear liquid from any sediment which may be present. Moisten strips of unsized paper with this solution, and dry them in the air. Keep this paper in a well-stoppered bottle.

The Process of Titration.—To perform the titration, withdraw 25 c.c. of the freshly-shaken bleaching-powder solution by means of a pipette, and allow it to flow into a beaker. Fill a 50 c.c. burette with the arsenite solution, after rinsing it out with the same solution. Allow the liquid to flow out until the meniscus stands at the zero graduation, making sure that the rubber joint, or the tap, contains no air-bubbles.

Now allow the arsenite solution to flow gradually and with continuous stirring into the 25 c.c. of bleaching-powder liquid. Take out a small drop of the liquid from time to time by means of a glass rod, and bring it into contact with a moistened strip of the starch-iodide-paper, placed on a white tile. As soon as a blue coloration ceases to be produced upon the paper, the determination is finished. The volume of liquid which has flowed from the burette is then read off.

Two titrations should be made, and they should not differ from one another by more than $\frac{1}{10}$ c.c.

From the volume of arsenite solution required for the titration, the weight of available chlorine present in the 10 grams of bleaching-powder may be calculated, and from this the percentage weight of available chlorine present in the bleaching-powder is deduced.

The Following Example is a record of the results which were obtained in an estimation, together with the calculation of the percentage of "available chlorine" present in the bleaching-powder:—

10 grams of bleaching-powder were treated with water and made up to 1 litre.

25 c.c. of this liquid required 20·7 c.c. of the arsenite solution.

Since 1 c.c. of the arsenite corresponds to 0·003545 gram of Cl, the weight of Cl in 25 c.c. of the bleaching-powder liquid $= 20{\cdot}7 \times 0{\cdot}003545 = 0{\cdot}07338$ gram.

Now the 25 c.c. of the liquid titrated correspond to 0·25 gram of bleaching-powder; therefore the percentage weight of available chlorine

$$= \frac{0{\cdot}07338 \times 100}{0{\cdot}25} = 29{\cdot}36.$$

Another Method for estimating the available chlorine in bleaching-powder is given in paragraph **293**.

USE OF POTASSIUM DICHROMATE SOLUTION.

252. When potassium dichromate solution is acidified, it readily imparts a portion of its oxygen to various substances, and is itself reduced to a salt of chromium which remains mixed with a salt of potassium. Advantage is taken of this property, in the estimation of ferrous salts, and of other oxidisable substances.

253. Thus if a solution of a ferrous salt is acidified with a dilute acid, it is at once converted into a ferric salt by the addition of potassium dichromate solution in sufficient quantity. The reaction is thus represented :—

$$6FeSO_4 + K_2Cr_2O_7 + 8H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 2KHSO_4 + 7H_2O.$$

From this it is seen that 294·68 parts of potassium dichromate convert $6 \times 56 = 336$ parts of iron from the ferrous into the ferric state.

Now, since potassium dichromate is reddish-yellow, and deoxidation converts it into a bluish-green chromium salt, the point at which a slight excess of dichromate has been added to the ferrous salt cannot readily be seen.

The precise point of completion of the change of ferrous into ferric salt in the above reaction is therefore ascertained by means of freshly-made potassium ferricyanide solution. Ferrous salts give a blue precipitate with this reagent; while ferric salts give no blue precipitate. The dichromate solution is accordingly added to the acidified iron solution, until a drop of the latter ceases to give a blue coloration, when it is brought into contact with a drop of potassium ferricyanide solution which has been placed on a white tile.

Preparation and Standardisation of Potassium Dichromate Solution.

254. Heat about 100 grams of pure recrystallised potassium dichromate gently in a porcelain dish until the salt is fused. Allow the salt to cool, and then powder it in a clean dry mortar. Weigh out $\frac{294{\cdot}68}{60} = 4{\cdot}91$ grams of the powdered dichromate into a litre-flask. Dissolve it in distilled water, and fill up the flask to the mark with water. Then mix the liquid by shaking it well. Each c.c. of this solution corresponds approximately to $\frac{56}{10 \times 1000} = 0{\cdot}0056$ gram of iron.

This solution may be considered to be of the true strength only when it is freshly prepared. It will require to be standardised afresh, after it has been kept for some time.

When it is necessary to ascertain the strength of the dichromate solution, a solution of ferrous sulphate of known strength is required. This is prepared either from a weighed quantity of metallic iron, or from a known weight of ferrous ammonium sulphate.

255. Titration of the Dichromate Solution by means of Metallic Iron.—For this process it is necessary to dissolve a known weight of pure iron in dilute sulphuric acid without contact with air.

Preparation of the Solution of Iron.—Weigh out accurately about 1 gram of pianoforte wire, free from rust, and cut it into pieces about 1 inch in length.

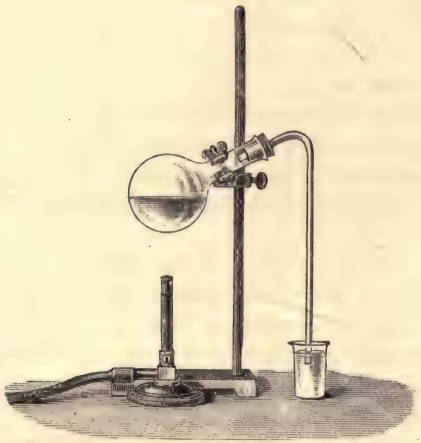
Fit into a 10-oz. round flask a perforated cork, through which a bent glass delivery-tube passes (fig. 71). One end of this tube terminates just below the cork, while the other end dips beneath the surface of a little water contained in a small beaker. Clamp the flask in an inclined position upon a retort-stand.

Now half fill the flask with dilute sulphuric acid, drop in

a small piece of pure crystallised sodium carbonate, and replace the cork and tube. The carbonate will dissolve, evolving carbon dioxide, which will replace the air in the flask. When the effervescence has nearly ceased, add the weighed steel wire. Then fit in the cork and tube, and arrange the apparatus as is shown in fig. 71. Apply a gentle heat by means of a small flame, and continue heating until the wire is dissolved.

While the operation of solution is proceeding, prepare some cold water free from dissolved oxygen, by boiling some

FIG. 71.



distilled water for a few minutes, and then cooling it rapidly by immersing the flask in cold water.

As soon as the process of solution of the iron wire is completed, cool the solution, transfer it rapidly to a 250 c.c. flask, and rinse out the round flask several times into the measuring-flask with the above air-free water. Finally, make up the solution to the mark with the air-free water.

256. *The Process of Titration.*—The titration may now be performed. Fill a 50 c.c. burette to the zero mark with the potassium dichromate solution. Measure out 25 c.c. of the

iron solution into a 10-oz. flask, dilute it with about twice its volume of air-free water, and add a few drops of strong sulphuric acid. Place a number of drops of a very dilute and freshly-prepared potassium ferricyanide solution upon a white tile by means of a glass rod. Then allow the solution of dichromate to run from the burette into the flask, mixing well after each addition.

From time to time take a drop of the iron solution out of the flask by dipping into the liquid a clean glass rod, and bring the drop into contact with one of the drops of potassium ferricyanide solution on the tile. The first few drops from the flask will cause a strong blue coloration of the ferricyanide. But as the addition of the dichromate proceeds, the colour produced in the ferricyanide will become more faint. As soon as the coloration becomes very faint, the addition of the dichromate solution must be continued very cautiously, until a drop of the liquid just ceases to produce a blue coloration with the ferricyanide. The volume of the dichromate solution, which has been allowed to flow from the burette, is then read.

Two more similar titrations should then be made. In each of these, nearly the whole volume of dichromate solution required should be allowed to flow into the flask at once from the burette, the last half of a c.c. only being gradually added drop by drop. The results of these titrations should not differ by more than the tenth of a c.c.

In calculating the strength of the solution from these results, the weight of iron contained in the solution used in the titration must be multiplied by 0·996, in order to correct it for impurities present in the steel wire originally employed; and from the weight of pure iron thus found, the exact strength of the standard solution of dichromate may be calculated.

The Following Example will serve to illustrate the process of calculation :—

1·152 grams of steel wire were dissolved, as is described above, and were made up to 250 c.c.

25 c.c. of this solution required 21·1 c.c. of dichromate solution.

Therefore 211 c.c. of dichromate solution correspond to 1·152 grams of steel wire.

And 1000 c.c. of dichromate solution will therefore correspond to $\frac{1{\cdot}152 \times 1000}{211} = 5{\cdot}4598$ grams of steel, which contain $5{\cdot}4598 \times 0{\cdot}996 = 5{\cdot}4379$ grams of *pure* Fe.

Each c.c. of the dichromate solution is therefore equivalent to 0·005438 gram of Fe.

257. Titration of the Standard Dichromate Solution by means of Ferrous Salt.—The standard iron solution for titrating the dichromate may also be prepared from ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2.6H_2O$.

For this purpose 7 grams of the salt are accurately weighed out. This is dissolved in air-free water, and is then made up to 250 c.c.

The above weight of the salt will give a solution containing 4 grams of iron per litre, since the double salt contains one-seventh its weight of iron.

The process of titration is performed in exactly the same way as has been already described (**256**), a few drops of strong sulphuric acid being added to the iron solution before the dichromate solution is allowed to flow in.

Estimation of Iron in an Iron Ore by means of Dichromate.

258. The estimation of the total amount of iron present in the ore may be effected by means of the standard potassium dichromate solution, as is described below. If ferrous compounds have been found by a qualitative test, their estimation is provided for in pars. **268** and **269**.

259. Process of Solution of the Iron.—Weigh out accurately about 2·5 grams of the powdered iron ore, which has been prepared as has been already described (**33–35**). Heat this for about half an hour with hydrochloric acid, diluted with its own volume of water, in a covered beaker

over a small flame. Dilute this solution *slightly* with water, allow the undissolved matter to subside, and decant the liquid through a filter.

Then treat the residue again with a small quantity of dilute acid, and decant the liquid through the same filter as before. This procedure will usually extract all the iron from the ore. But if, on treating the residue with a small additional quantity of acid and filtering, iron can be detected in a drop of the acid filtrate by a decided coloration with KCyS solution, the ore must be treated again with acid, This treatment must be repeated until no more iron is found in the last extract. The residue is now transferred to the filter, and is washed with as small a quantity of water as possible, and the filtrates and washings are mixed together, and constitute the "iron solution."

The iron present in this solution must then be reduced to the ferrous condition before being titrated. Three methods of reduction are described below, in which zinc, solution of stannous chloride, and ammonium bisulphite are added respectively as reducing agents.

260. Process of Reduction by means of Zinc.—The iron solution is transferred to the flask shown in fig. 71 (p. 185). The liquid must, if necessary, be first evaporated until it does not more than half fill the flask. Strong hydrochloric acid is then added, and granulated zinc free from iron is dropped into the flask. The zinc will dissolve in the acid, with evolution of hydrogen, and a portion of the nascent hydrogen will act upon the ferric chloride, and will reduce it to ferrous chloride. At the same time the colour of the solution will change from yellow to pale green. After a time it will be necessary to heat the liquid gently in order to promote the action. The heating should be continued until all the zinc is dissolved.

Before proceeding to estimate the iron, ascertain that it is present entirely in the ferrous state, by taking out a drop of the solution with a clean glass rod, and bringing it into contact

with a drop of potassium sulphocyanide solution on a white tile or dish. No red colour, or only a *very faint* pink tint, should appear. If a distinct red colour is produced, more zinc and hydrochloric acid should be added, and the process must be continued in the reduction apparatus until all the zinc has dissolved. The solution is then again tested with the sulphocyanide, and these operations are repeated until no ferric salt can be detected.

When the whole of the iron has thus been proved to be present in the solution in the ferrous state, the liquid is quickly cooled, and is made up at once to 250 c.c. with air-free water. The titration of 25 c.c. of this solution is then immediately proceeded with in the acidified liquid, as has been already described (**256**), and is completed with as little delay as possible.

From the volume of dichromate solution which is used in the titration, the quantity of iron present, and its percentage in the ore, may be calculated as is shown in **256**.

261. Process of Reduction by means of Stannous Chloride Solution.—The iron in the acidified iron solution is reduced to the ferrous state by the addition of stannous chloride solution, which must be added in slight excess. The excess of the stannous salt is then removed by adding excess of mercuric chloride solution :—

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2.$$

This method is not suitable for iron solutions which are coloured brown with organic matter.

The iron solution (**259**) is made up to 250 c.c. 25 c.c. are placed in a 4-oz. flask, 2 c.c. of strong hydrochloric acid are then added, and the liquid is heated to boiling. Clear, freshly-made stannous chloride solution (1 : 25) is next added from a pipette. The stannous solution is added drop by drop, until the yellow colour of the iron solution just disappears. About 3 c.c. of a saturated solution of mercuric chloride are then added. This must produce turbidity in the liquid, indicating that the stannous chloride solution has

been added in excess. The solution is then cooled to about 60° C., and is titrated with the potassium dichromate solution (256).

Note.—Care must be taken that a large excess of $SnCl_2$ solution is not added, else a much larger quantity of $HgCl_2$ solution will be required, and the precipitate of Hg_2Cl_2 will interfere with the titration.

262. Process of Reduction by means of Ammonium Bisulphite Solution.—Prepare some ammonium bisulphite solution by passing SO_2 gas into strong ammonia solution. Continue to pass the gas until the crystals, which form at first, are redissolved, and the liquid smells strongly of SO_2. The SO_2 gas may be conveniently supplied from a bottle of the liquid SO_2.

Pour the ferric solution, which should not exceed 100 c.c. in volume, into a small flask covered with a funnel, and add ammonium hydrate gradually until a slight permanent precipitate is formed. Then add the bisulphite solution to it in the proportion of 5 c.c. to each gram of ore taken. Place some pieces of platinum wire in the flask to prevent bumping, shake the liquid vigorously, and heat gently. Gradually increase the heating until the solution boils. If any precipitate forms at first, it will redissolve, and the liquid will gradually lose its yellow colour.

As soon as the liquid is colourless, add H_2SO_4 diluted with twice its weight of water, in the proportion of 30 c.c. to each 5 c.c. of bisulphite solution which was previously added. Boil the liquid until all the SO_2 is driven off, make it up to 250 c.c., and titrate the ferrous salt (256) in 50 c.c. of this solution.

USE OF POTASSIUM PERMANGANATE SOLUTION.

263. Potassium permanganate solution readily yields up a portion of its oxygen under suitable conditions to certain substances, and may therefore be used instead of potassium

dichromate solution for many volumetric estimations. Potassium permanganate, however, cannot be used for the estimation of a substance in the presence of organic matter, and its indications are not trustworthy if any large amount of hydrochloric acid is present.

Solution of potassium permanganate, moreover, if exposed to light, becomes gradually weaker by the decomposition of the salt. This change may be almost entirely prevented by keeping the solution in a *dark blue* Winchester quart-bottle, and by storing it in a cool and dark place. Owing to its liability to change, the permanganate solution always requires to be standardised immediately after its preparation, as well as at frequent intervals when it is stored.

Preparation, Standardisation, and use of Potassium Permanganate Solution.

Potassium permanganate solution is usually standardised by means of a ferrous salt in an acid solution. It can, however, also be standardised by means of oxalic acid.

264. Titration of the Permanganate Solution by means of Ferrous Salt.—The following reaction takes place when a ferrous salt is used in the titration:—

$$K_2Mn_2O_8 + 10FeSO_4 + 9H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + 2KHSO_4 + 8H_2O.$$

The ferrous sulphate solution should be made immediately before it is required for the titration by dissolving iron wire in dilute sulphuric acid, or by dissolving ferrous ammonium sulphate in water. The procedure is the same as that already described under the standardisation of potassium dichromate (255–257); but the use of an indicator is unnecessary, since the end of the reaction is easily seen by the appearance of a pink tint in the liquid, as soon as the permanganate is present in excess.

Dissolve about 5 grams of potassium permanganate in water, and dilute this solution to 1 litre.

265. Pour some of the permanganate solution into a burette with a glass stop-cock (fig. 66, p. 158), filling the burette to the zero mark. An india-rubber joint must not be used in the burette, as it would reduce the permanganate. Allow the permanganate solution to flow into the ferrous solution, which has been acidified with a few drops of strong sulphuric acid, and has been diluted with freshly-boiled and cooled distilled water. Continue the addition of the permanganate solution until a faint permanent pink colour remains after the liquids have been well mixed. This colour is readily seen, if the beaker containing the iron solution is placed upon a piece of white paper, or upon a white tile, or if the titration is performed in a porcelain dish. Two titrations should be made, and they must not differ by more than one-tenth of a c.c.

From the number of c.c. of the permanganate solution which are used, the strength of the solution may be calculated. This is stated either in terms of metallic iron as has been described in the standardisation of potassium dichromate, or in terms of available oxygen.

In the latter case one atom of oxygen corresponds to two atoms of iron in the ferrous state, since $2FeO + O = Fe_2O_3$. Hence every 112 parts of iron oxidised correspond to 16 parts of oxygen, and from this relation the oxygen-value of the potassium permanganate is easily calculated.

266. Titration of Potassium Permanganate Solution by means of Oxalic Acid.—When potassium permanganate solution is added to a warm solution of oxalic acid which has been acidified with sulphuric acid, the following reaction takes place :—

$$5H_2C_2O_4.2H_2O + K_2Mn_2O_8 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 18H_2O.$$

It will be seen, on comparing this equation with that given for ferrous salt (**264**), that 126·02 parts of crystallised oxalic acid are equivalent to 112 parts of iron, and require 16 parts of oxygen for their complete oxidation.

This relation is shown more simply by the following equation :—$H_2C_2O_4.2H_2O + O = 2CO_2 + 3H_2O$.

A Deci-normal Solution of pure recrystallised oxalic acid (**71**) will be required for the titration. This is prepared by dissolving 6·301 grams of the dry crystals in water, and making the solution up to 1 litre.

Fifty c.c. of this solution are measured out into a beaker by means of a pipette, a little sulphuric acid is added, and the liquid is considerably diluted with water. The diluted solution is now heated to 60° C., and solution of potassium permanganate, containing about 5 grams per litre, is gradually added, until a faint permanent pink tint remains in the liquid after it has been stirred. If the permanganate is added too rapidly, a brown precipitate forms, which is removed with difficulty by adding more sulphuric acid.

The strength of the permanganate solution is readily calculated from the proportions yielded by the above equation.

267. A Solution which is to be Titrated by means of Potassium Permanganate Solution must always be first acidified by means of sulphuric acid. Nitric acid should not be present in any quantity. Hydrochloric acid is liable to be oxidised by the permanganate, and to evolve chlorine, unless it is very considerably diluted : and this change interferes with the accuracy of the result.

Organic matter also reduces the permanganate, and destroys the accuracy of the determination.

Bearing in mind the above precautions, however, potassium permanganate may be used for estimating many substances. Some of these processes are described below.

Estimation of Iron in Ferrous and Ferric Compounds by means of Permanganate.

The process of titration by means of ferrous salt (**264**) may be adapted to the estimation of iron when it is present

in a substance wholly in the ferrous or the ferric condition, or partly in both conditions. The weight of Fe is calculated from the equation in paragraph **264**, from the result of the titration.

268. Estimation of Iron in Ferrous compounds.—Care must be taken that the iron is not exposed to oxidation and conversion into ferric salt during the process of solution. This will be prevented by adopting the method of solution which is described in par. **255**. The titration is carried out as is directed in par. **265**.

Substances which do not give the iron in solution by treatment with sulphuric acid are fused with $KHSO_4$ in Rose's crucible (**60**), and are then treated as above.

269. Estimation of the Total Iron in Ferric compounds, and in a mixture of Ferrous and Ferric compounds.

The ferric compound present in the solution is reduced to the ferrous state (**260–262**), and the iron is then titrated with permanganate (**265**).

If the solution of the original substance contains ferrous as well as ferric compounds, the iron in the ferrous compounds may be first estimated by titration in a part of the original solution (**268**). The total amount of iron is then estimated in another part of the original solution by reduction (**260, 262**) followed by titration, and the weight of iron in the ferric compounds which were orginally present in the substance is equal to the difference between the total percentage of iron, minus the percentage of iron present in the ferrous state.

The amount of iron in an iron ore, which yields up all its iron to sulphuric acid, may be estimated by means of permanganate. But if hydrochloric acid must be used in extracting the iron, or if organic matter is present, the titration must be made with potassium dichromate solution (**256**).

Estimation of Oxalate in Solution by means of Permanganate.

270. Oxalates which are soluble in water are readily estimated by means of permanganate. About 5 grams of the oxalate are accurately weighed and dissolved in water. The solution is then made up to 250 c.c. A suitable quantity of this solution is acidified with sulphuric acid, and is titrated as was described in paragraph **266**.

The weight of (C_2O_4) present may be calculated from the equation in paragraph **266**.

Estimation of Calcium in Solution by means of Permanganate.

271. The calcium is completely precipitated by adding an excess of standard oxalic acid solution. The excess of oxalic acid is then determined by titration with standard potassium permanganate solution (**272**); or, if the quantity of calcium present is considerable, the oxalic radicle present in the calcium oxalate precipitate is estimated (**273**).

Add to the solution of the calcium compound, contained in a flask, a measured quantity of normal oxalic acid solution. The oxalic acid must be more than sufficient to precipitate all the calcium as oxalate. Add ammonium hydrate solution in excess, then boil the liquid and allow it to cool.

272. Titration of the Excess of Oxalic Acid added.—Transfer the liquid containing the precipitate of calcium oxalate to a suitable measuring-flask, make up to the mark with water, and mix the contents of the flask thoroughly. Pour this liquid through a dry filter into a flask of half the above capacity, filling the flask to the graduation mark.

Measure out an aliquot part of the filtrate—say one-half. Acidify this with sulphuric acid, heat the liquid to 60° C.,

and determine the oxalic acid in it by means of potassium permanganate solution (**266**).

Calculate from this result the weight of oxalic acid in the whole of the filtrate, and subtract this weight from that of the oxalic acid which was originally added for the precipitation of the calcium. The remainder will be the weight of oxalic acid which is chemically equivalent to the calcium present, and from this the weight of Ca may be calculated.

273. Titration of the Oxalic Acid which has been Precipitated by the Calcium.—If the calcium oxalate precipitate is large in amount, it is filtered and is well washed on the filter. It is then dissolved in a small quantity of warm hydrochloric acid, and the solution is diluted with water. This liquid is mixed with a little sulphuric acid and heated to 60° C.; it is then at once titrated by the potassium permanganate solution. The quantity of oxalic acid thus found is chemically equivalent to the calcium originally present, 126·02 parts of oxalic acid ($H_2C_2O_4.2H_2O$) representing 40 parts of calcium.

Estimation of Lead in Solution by means of Permanganate.

274. Lead may be estimated in the same way as is described for the estimation of calcium (**271, 272**). If the second method of titration (**273**) is employed for this estimation, the lead oxalate precipitate must be dissolved in dilute nitric acid; sulphuric acid is then added, and the oxalic acid is titrated. 126·02 parts of oxalic acid ($H_2C_2O_4.2H_2O$) represent 206·91 parts of lead.

USE OF STANDARD IODINE SOLUTION.

275. Iodine dissolved in potassium iodide solution may be used for many different volumetric determinations. The chemical reaction on which the estimations are based is usually that of oxidation, as is the case in the estimation of arsenious oxide :—$As_2O_3 + 2H_2O + 2I_2 = As_2O_5 + 4HI$.

If the iodine solution is used in conjunction with sodium thiosulphate solution, the number of estimations to which it

is applicable is increased. In these cases the iodine solution is usually added in excess, and the excess of iodine is then estimated by means of the sodium thiosulphate solution. The following equation represents the reaction which takes place :—$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$.

In titrating the iodine solution by means of the thiosulphate solution, the completion of the process is indicated by the blue colour which iodine gives with starch. When sodium thiosulphate solution is gradually added to iodine solution, the brown colour of the iodine solution will slowly change to yellow, and finally the liquid will become colourless; but the exact point at which the yellow colour of the solution disappears is difficult to judge with precision.

If, however, a few drops of starch solution are added to the pale yellow liquid, an intense blue colour is produced, which entirely disappears on the addition of more thiosulphate solution. In this case the completion of the titration is very sharply defined by the disappearance of the blue colour.

Occasionally the process of titration is reversed, and the completion of the reaction is shown by the appearance of the blue colour.

Preparation and Standardisation of the requisite Standard Solutions.

The following solutions are required for the processes of estimation involving the use of standard iodine and standard sodium thiosulphate solutions :—A deci-normal solution of iodine; a deci-molecular solution of sodium thiosulphate; and a dilute solution of starch.

276. Preparation of the Deci-normal Solution of Iodine.—This solution should contain $\frac{126{\cdot}86}{10} = 12{\cdot}686$ grams of pure iodine per litre.

Weigh out accurately into a litre-flask from a stoppered bottle 12·686 grams of pure iodine (**74**, Exp. 27), taking care

to remove the bottle from the balance-case before taking out the stopper. Then add about 30 grams of pure potassium iodide and about 250 c.c. of water. Shake the contents of the flask until complete solution has taken place; add more KI if necessary to complete the solution of the iodine. Then fill the flask up to the mark with distilled water.

This solution must be kept in a well-stoppered bottle, and in a cool place.

Since iodine is very volatile, it is difficult to weigh out exactly the quantity which is required for making a litre of the standard solution. Hence about 13 grams may be accurately weighed out by difference. This is dissolved in the manner already described, and is made up to the volume which is necessary to furnish a solution of deci-normal strength. Thus, if 12·5 grams were weighed out, the volume of the iodine solution required would be $\frac{1000 \times 12{\cdot}5}{12{\cdot}686} = 985{\cdot}3$ c.c.

277. Preparation of the Deci-molecular Solution of Sodium Thiosulphate.—The solution must contain $\frac{248{\cdot}27}{10}$ $= 24{\cdot}827$ grams per litre of the pure recrystallised salt, $Na_2S_2O_3.5H_2O$.

Weigh out accurately 24·827 grams of the pure recrystallised salt, which has been powdered and then dried by pressure between filter-paper. Dissolve this in water, and dilute the solution to 1 litre in the measuring-flask or cylinder.

The solution undergoes chemical change by the action of light, hence it must be kept in a dark blue Winchester quart-bottle, in a closed cupboard, the interior of which is painted dead-black. Even when these precautions against exposure to light are taken, the solution will require frequent titration (280).

278. Preparation of the Starch Solution.—Make about 1 gram of starch, free from acid, into a thin cream with a small quantity of cold water. Pour this into about 100 c.c. of water boiling in a porcelain dish, and continue the boiling for a few minutes. Allow the liquid to stand until it is

cold, and pour off the clear solution. It is necessary to prepare the starch solution immediately before it is used, since starch solution which has been prepared for some time is far less sensitive to iodine than when it is freshly made.

279. Process of Standardising the Iodine and Thiosulphate Solutions.—If the thiosulphate solution only is to be standardised the process described in par. **280** may be employed.

Usually it is only necessary to determine the *relative values* of the iodine and the thiosulphate solutions.

It will often happen that 1 c.c. of the thiosulphate solution is not exactly equivalent to 1 c.c. of the iodine solution. Hence it is necessary to ascertain the relative strengths of the two solutions in the following manner.

Measure 20 c.c. of the iodine solution into a beaker, and dilute it with water. Then add the thiosulphate gradually from a burette, until the colour of the liquid fades to a pale yellow tint. Now add a few drops of the starch solution, and continue the titration until the blue colour thus produced just disappears.

The iodine solution should require the addition of 20 c.c. of thiosulphate solution. If more or less than this volume is required, the factor necessary to correct the volume should be noted on the label, the iodine solution being taken as the standard.

Thus, if 20·2 c.c. of the thiosulphate solution are required for 20 c.c. of the iodine solution, each c.c. of the thiosulphate solution will be equivalent to $\frac{20}{20 \cdot 2} = 0 \cdot 99$ c.c. of the iodine solution. Hence the number of c.c. of thiosulphate solution used in any estimation will require to be multiplied by 0·99, in order to ascertain the corresponding volume of the iodine solution. The number 0·99 is termed the factor of the solution, and is entered as such upon the label of the bottle.

280. The Thiosulphate Solution may be Standardised by adding it to the standard solution of potassium dichromate (**254**) or of potassium permanganate (**264**), which has been mixed with excess of KI solu-

tion and has then been acidified with HCl and H_2SO_4 respectively. The following are the reactions upon which the titration depends:—

$$K_2Cr_2O_7 + 6KI + 14HCl = 3I_2 + 8KCl + Cr_2Cl_6 + 7H_2O.$$

$$K_2Mn_2O_8 + 10KI + 8H_2SO_4 = 5I_2 + 8H_2O + 2MnSO_4 + 6K_2SO_4.$$

It will be seen that iodine is liberated in proportion to the weight of $K_2Cr_2O_7$ or of $K_2Mn_2O_8$, which is present.

Estimation of Antimony in Tartar-emetic by means of Iodine.

281. When iodine is added to an alkaline solution containing Sb_2O_3, the following reaction takes place:—

$$Sb_2O_3 + 2I_2 + 2H_2O = Sb_2O_5 + 4HI.$$

Since free hydriodic acid is formed in this reaction, sufficient alkali must be added to neutralise this acid. A normal alkaline carbonate affects iodine, hence a bicarbonate must be employed for the neutralisation. For every decigram of Sb_2O_3 present in the liquid, about 25 c.c. of a saturated solution of $NaHCO_3$ should be added.

Weigh out accurately about 1·5 grams of anhydrous tartar-emetic, $KSbOC_4H_4O_6$ (**73**, Exp. 26), dissolve it in water, and dilute the solution to 250 c.c. Transfer 25 c.c. of this solution to a beaker, and add an equal volume of a cold saturated solution of $NaHCO_3$ free from Na_2CO_3. Now pour in a few drops of starch solution (**278**), and add the iodine solution from a burette *provided with a glass stopcock*, until a faint blue colour just appears. The blue colour disappears when the liquid is stirred, and the first appearance of a *permanent blue tint* is taken as indicating the completion of the reaction.

The amount of Sb_2O_3 present can be calculated from the above equation, when the amount of iodine required for its oxidation is known.

The above method is also applicable to the estimation of antimonious oxide. The oxide is first dissolved in tartaric acid and water. The tartaric acid is then exactly neutralised by means of NaOH solution, the requisite quantity of $NaHCO_3$ is added, and the titration is performed as is described above.

Estimation of Arsenic in Arsen*ious* and Arsen*ic* Oxides, and in their Compounds, by means of Iodine.

282. When iodine is added to an alkaline solution of As_2O_3, the following reaction takes place:—

$$As_2O_3 + 2I_2 + 2H_2O = As_2O_5 + 4HI.$$

If the process of estimation, which is based on this reaction, is to be applied to the higher oxide As_2O_5, that oxide must be reduced to As_2O_3 by passing SO_2 gas to saturation into the solution. The excess of SO_2 gas is then driven off by boiling, and the solution of As_2O_3 is titrated as is described below.

If both oxides of arsenic are present, the As_2O_3 alone is first estimated in part of the solution. A fresh portion of the original solution is then reduced by sulphurous acid as is described above, and the As_2O_3 is titrated: the total amount of As present in the original solution is thus estimated as As_2O_3. From these two determinations the amount of As_2O_3 and of As_2O_5 which were originally present are easily calculated.

For practice in the estimation, weigh out accurately about 1·5 gram of commercial sodium arsenate, and dissolve it in about 150 c.c. of water. Add a little acetic acid and sodium acetate to the solution, and boil for ten minutes, in order to destroy any nitrites which may be present. Cool the solution and dilute it to 250 c.c.

The amount of arsenious oxide in 25 c.c. of this solution is determined by mixing it with starch solution, and then adding standard iodine solution until a permanent blue coloration is formed.

The arsen*ic* oxide in 100 c.c. of the original solution is then reduced by treatment with excess of SO_2 gas, and the excess is removed by boiling. The solution is then cooled and made up to 200 c.c. The amount of As_2O_3 in 50 c.c. of this solution, that is, in 25 c.c. of the original solution, is found by titrating it with the iodine solution, after adding $NaHCO_3$ in moderate excess as is indicated by methyl-orange.

The difference between the two titrations gives the amount of As_2O_3 which was originally present as As_2O_5.

The oxides of arsenic may be estimated by this method. They are

first dissolved in HCl. This solution is exactly neutralised by NaOH solution, then mixed with $NaHCO_3$ solution, and is finally titrated with iodine solution.

Estimation of Stannous Chloride by means of Iodine.

283. When iodine solution is brought into contact with stannous chloride solution, the following reaction takes place :—$SnCl_2 + I_2 = SnCl_2I_2$.

On this reaction a process for estimating stannous salt by means of iodine is founded.

Dissolve about 1 gram of the tin salt, or of metallic tin, in hydrochloric acid. The air should be displaced from the vessel by a current of carbon dioxide gas, so as to prevent oxidation and formation of stannic salt from occurring during the process of solution. The solution of *metallic* tin may be hastened by the addition of pieces of platinum foil.

To this solution add Rochelle-salt solution, and then sodium bicarbonate solution in excess. More Rochelle-salt solution is added, if necessary, to render the solution clear.

Dilute the solution with water to 250 c.c., and titrate an aliquot part of it with deci-normal iodine solution, using starch as the indicator.

From the above equation it will be seen that 253·72 of iodine correspond to 190 of $SnCl_2$.

Estimation of Hydrogen Sulphide in Aqueous Solution by means of Iodine.

284. When a dilute solution of hydrogen sulphide is brought into contact with free iodine, the following reaction takes place :—$H_2S + I_2 = 2HI + S$. Hence in the exact conversion of I into HI by H_2S, 253·72 of iodine correspond to 34·07 of H_2S.

If the solution in which the H_2S is to be estimated by the above reaction contains more than 0·04 per cent. of the gas,

the change may not occur entirely according to the above equation.

Two methods of procedure are described below.

By the first (**285**) the hydrogen sulphide is directly titrated by adding the iodine solution under suitable conditions to the hydrogen sulphide solution until the reaction is completed.

In the second method (**286**) the iodine solution is at once added in excess to the hydrogen sulphide solution. The total volume of iodine solution added is known, and the excess is then estimated by means of thiosulphate solution.

The second method (**286**) is to be preferred on account of its greater accuracy; it prevents the hydrogen sulphide solution from undergoing loss of strength during the titration. This method may be advantageously applied to check the result previously obtained by the first method.

285. Direct Titration with Standard Iodine Solution.— Prepare some solution of H_2S, by passing the gas into water, and titrate a measured quantity of this liquid with deci-normal iodine solution. This titration will roughly indicate the volume of iodine solution required by the solution of H_2S.

If the quantity of hydrogen sulphide thus indicated in the solution is greater than 0·04 per cent., measure the rest of the solution. Then dilute it with air-free water until it contains less than 0·04 per cent., and titrate a measured volume of this solution with iodine. This titration will indicate very nearly the true amount of iodine solution required. But since loss of the gas will occur by escape into the air and by oxidation from the air, during the process of the titration, the results will be rather too low. This error may be avoided by proceeding as follows.

Introduce into a flask nearly the volume of the iodine solution which was required in the last titration: add to this the volume of diluted hydrogen sulphide solution then employed. This amount will destroy the colour of the iodine solution. Now add a little starch solution, and carefully add more iodine solution in measured quantity until a permanent blue colour is just obtained.

From the total volume of iodine solution used, the amount of hydrogen sulphide can be calculated by means of the equation (284).

286. Addition of the Hydrogen Sulphide Solution to Excess of Standard Iodine Solution and Titration of the Excess.—Greater accuracy is attained by first diluting the hydrogen sulphide solution, if necessary, until it contains not more than 0·04 per cent. of the gas (285), and then adding a measured volume rapidly to an excess of the standard iodine solution, the volume of which must be accurately known. The presence of the iodine in excess is indicated by a permanent yellow colour remaining in the liquid after it has been stirred.

The excess of iodine present in the liquid is then estimated by means of standard sodium thiosulphate solution in the presence of starch solution (279).

Estimation of Sulphur Dioxide in Aqueous Solution by means of Iodine.

287. If a *dilute* solution of sulphur dioxide gas is mixed with iodine solution, the following reaction takes place:—

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI.$$

The solution, however, must not contain more than 0·05 per cent. of sulphur dioxide, if the reaction is to be of a definite character: and it is also necessary to insure the presence of an excess of iodine during the titration.

Two methods of procedure may be adopted. The second method (289) is to be preferred when great accuracy is required: it may be applied to check the result obtained by the less accurate method which is described first (288).

It will be seen from the above equation that 253·72 of iodine correspond to 64·06 of SO_2.

288. Dilute 10 c.c. of the ordinary solution of sulphurous acid to 1 litre by the addition of air-free water. Fill up the

burette with this solution, and add it rapidly to a known quantity of the iodine solution. As soon as the iodine solution has faded to a pale straw colour, add a little starch solution, and continue the addition of the sulphur dioxide solution until the blue colour just disappears.

289. Greater accuracy is attained by adding a definite quantity of the sulphur dioxide solution to a measured volume of the iodine solution. The iodine solution must be in excess; this is shown by the colour of the liquid remaining after it has been well shaken. The excess of iodine is then titrated by sodium thiosulphate solution (**279**).

Estimation of (S_2O_3) in Thiosulphate by means of Iodine.

290. As has been already explained (**275**), a soluble thiosulphate undergoes a definite chemical reaction with iodine. Hence a thiosulphate may be estimated by means of standard iodine solution.

If the sodium salt, $Na_2S_2O_3.5H_2O$, is used, the reaction which takes place is as follows:—

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

For practice in the estimation weigh out accurately about 10 grams of sodium thiosulphate, dissolve this in water, and make up the solution to 1 litre. Titrate 20 c.c. of this solution with standard iodine solution, as is described in paragraph **279**.

USE OF STANDARD SODIUM THIOSULPHATE SOLUTION WITH POTASSIUM IODIDE.

Many substances have the power of liberating iodine from a solution of potassium iodide. Thus free chlorine

reacts upon potassium iodide solution in the following manner:—$Cl + KI = KCl + I$.

Since each substance will liberate its chemical equivalent of iodine, which is then easily estimated by standard thiosulphate solution (**279**, **280**), this reaction is frequently made use of in volumetric analysis.

When some substances are heated with hydrochloric acid, they liberate a definite proportion of chlorine. Thus, when manganese dioxide is heated with hydrochloric acid, the following change occurs:—$MnO_2 + 4HCl = Cl_2 + MnCl_2 + 2H_2O$. The chlorine, thus evolved, may be conducted into potassium iodide solution, when iodine is liberated as is described above. The amount of iodine liberated will be equivalent to the chlorine, and is therefore proportionate to the available oxygen present in the manganese dioxide.

The quantity of iodine liberated is determined by titration with standard sodium thiosulphate solution and starch (**279**).

Estimation of Chlorine and Bromine in Aqueous Solution by means of KI and Thiosulphate.

291. Mix a measured quantity of dilute chlorine solution with solution of potassium iodide. Take care that an excess of potassium iodide is employed, as is shown by the liquid remaining brown or yellow in colour after it has been well mixed. (See *Note.*)

Then determine the amount of free iodine by titration with standard sodium thiosulphate solution (**279**).

In calculating the weight of chlorine present, it must be remembered that 35·45 of chlorine liberate 126·86 of iodine.

Note.—The most satisfactory way of insuring the presence of potassium iodide in excess is to mix the chlorine solution with the potassium iodide solution as has been directed above. An aliquot part of this liquid is then removed and titrated with the standard thiosulphate solution. An equal volume of the liquid is then mixed with additional potassium iodide solution, and is titrated with the

thiosulphate. If the two titrations yield identical results, the potassium iodide solution was originally present in excess.

Estimation of Bromine in Aqueous Solution.

292. The bromine solution is diluted, and is added to an excess of potassium iodide solution (*Note*, **291**). The iodine, which is liberated by the bromine, is then titrated by standard thiosulphate solution (**279**). In calculating the weight of bromine present in the original solution, it must be remembered that the 79·96 of bromine liberate 126·86 of iodine.

Estimation of the "Available Chlorine" in Bleaching-Powder by means of KI and Thiosulphate.

Note.—Refer to **250** for an explanation of the term "available chlorine."

293. The turbid solution of bleaching-powder is prepared in the manner described in paragraph **251**. After this liquid has been well mixed by shaking, transfer 25 c.c. of it to an 8-oz. beaker: add an excess of potassium iodide solution (*Note*, **291**), and acidify the liquid with dilute hydrochloric acid. Then determine the amount of iodine which is liberated, by means of sodium thiosulphate solution and starch (**279**).

The amount of available chlorine in the bleaching-powder is chemically equivalent to the iodine liberated, 35·45 of chlorine corresponding to 126·86 of iodine.

Another Method of Estimation is described in **251**.

Indirect Estimation of Manganese Dioxide by means of KI and Thiosulphate.

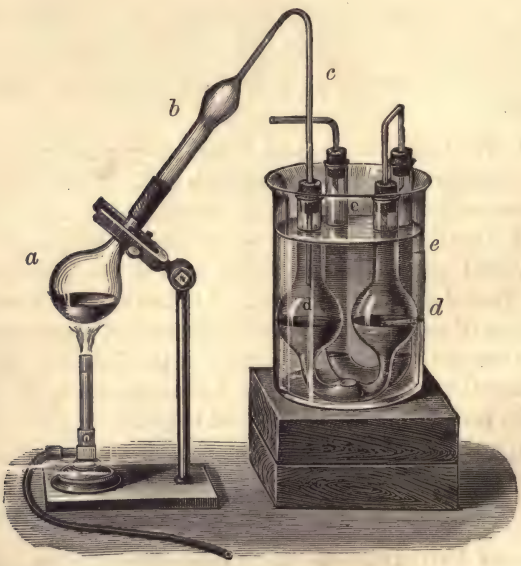
294. The manganese dioxide is heated with excess of hydrochloric acid, and chlorine gas is evolved. This gas is conducted into an excess of potassium iodide solution, and the iodine which is set free is estimated by means of standard sodium thiosulphate and starch solutions (**279**). It will be evident that 87·05 parts of MnO_2 will liberate 70·9 parts of chlorine and 253·72 parts of iodine.

295. The Apparatus, which is shown in fig. 72, will be found useful for carrying out the above process of estimation. It is prepared as follows.

Note.—The following apparatus involves the use of corks: these are advantageously dispensed with in some forms of absorption apparatus which are made entirely of glass.

A small flask or bulb-tube (*a*), of about 2 oz. capacity, is connected with a tube (*b*) by means of a black rubber joint,

FIG. 72.



in which the glass tubes are brought into contact with one another.

Upon the end of *b* is fused a thinner tube (*c*), which is bent as is shown in the figure, and is fitted to the bulbed U-tube (*d*) by means of a rubber cork. This apparatus will be found sufficient for ordinary purposes. But in the figure an additional plain U-tube (*e*) is shown, which may be used as a guard-tube to prevent the escape of any trace of chlorine.

These U-tubes are kept cool by immersing them in cold water contained in a beaker.

A plain bent glass tube of the same diameter throughout as the neck of the flask may replace the tubes (*b*) and (*c*). The rubber corks and connections, which are used in fitting up this apparatus, should be freed from sulphur by boiling them in sodium hydrate solution.

296. The Estimation is carried out as follows. Weigh out accurately about half a gram of fine-powdered manganese dioxide into the flask (*a*). Half fill the bulbs of the U-tube (*d*) with strong potassium iodide solution. If the second U-tube (*e*) is also used, pour into it sufficient potassium iodide solution to fill the bend. Ascertain that the apparatus is air-tight, and then add about 20 c.c. of strong hydrochloric acid to the manganese oxide in the flask.

It will be found convenient to introduce a small piece of magnesite with the manganese oxide. On the addition of the acid a regular stream of carbon dioxide gas will then flow through the U-tubes with the chlorine, and this will dilute the chlorine and render the absorption less violent.

Now heat the flask gently by means of a small flame: and as soon as the manganese dioxide is completely dissolved, boil the acid until all the chlorine has been expelled.

As soon as all the chlorine has passed into the absorption-tubes, pour out the contents of the first U-tube into a beaker, and rinse out the tube also into the beaker. If the potassium iodide solution in the second U-tube is yellow, the chlorine has not been completely absorbed by the first tube: the contents of the second tube must therefore also be transferred to the beaker. The free iodine in this solution is at once titrated by means of standard sodium thiosulphate solution and starch (279.)

The free iodine thus found is a measure of the chlorine which has been liberated by the manganese dioxide, and two atoms of chlorine correspond to one molecule of MnO_2, as has been already explained.

Indirect Estimation of Chromate by means of KI and Thiosulphate.

297. When potassium dichromate is heated with strong hydrochloric acid, the following reaction takes place :—

$$K_2Cr_2O_7 + 14HCl = 3Cl_2 + Cr_2Cl_6 + 2KCl + 7H_2O.$$

Accordingly the process and apparatus which has been already described (**294–296**) for the estimation of MnO_2 may also be applied to the estimation of chromate. It will be seen that 294·68 of $K_2Cr_2O_7$ yield 212·7 of chlorine, and will therefore correspond to 761·16 parts of iodine liberated. Hence, when the amount of iodine liberated has been estimated by sodium thiosulphate solution, the amount of chromate may be calculated.

Indirect Estimation of Chlorate, Bromate, or Iodate by means of KI and Thiosulphate.

298. When a chlorate is heated with excess of strong hydrochloric acid, a mixture of chlorine with oxides of chlorine is evolved. This mixture sets free an amount of iodine from potassium iodide which is equivalent to the total weight of chlorine present in the gases evolved.

Hence the above method (**294–296**) of titrating the iodine, which has been liberated, with thiosulphate and starch solutions, may be used for the estimation of chlorate.

The acid-radicle of a *chlorate* (ClO_3) liberates, under the above conditions, *six* atoms of iodine. 122·59 parts by weight of $KClO_3$ will therefore liberate $126{\cdot}86 \times 6 = 761{\cdot}16$ parts of iodine.

The corresponding acid-radicle of a *bromate* (BrO_3) or of an *iodate* (IO_3) liberates only *four* atoms $= 507{\cdot}44$ parts of iodine.

These data suffice for calculating the weight of chlorate, bromate, or iodate from the result obtained by titrating the iodine which it can liberate.

299. A Simpler Method of Estimation depends upon the fact that some substances may be estimated by the amount of iodine which they

liberate, when they are simply digested with strong hydrochloric acid and potassium iodide. The apparatus and procedure are thus much simplified. This process is specially suitable for the estimation of bromate and of iodate.

A four-ounce bottle, which is fitted with an accurately ground stopper, is selected. The bottle should be tested to ascertain that the stopper is air-tight. This may be done by completely immersing the tightly-stoppered bottle in hot water, when no air-bubbles should escape between the neck and the stopper. If the stopper is not air-tight, it must be made so by grinding it into the neck with very fine emery powder and water.

Weigh out from 0·2 to 0·5 gram of the substance into the bottle, add the requisite excess of strong hydrochloric acid and of potassium iodide solution. Fasten the stopper down by means of copper binding wire, and heat the bottle in the water-bath. As soon as the decomposition is complete, withdraw the bottle from the bath and allow it to cool. Then empty the contents into a beaker, dilute the liquid with water, and titrate the free iodine with sodium thiosulphate solution and starch (**279**).

Indirect Estimation of Copper in Solution by means of KI and Thiosulphate.

300. The process of estimation depends upon the following reaction :—$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4$.

The potassium iodide is added in excess to the copper solution, and the liquids are thoroughly mixed. The amount of free iodine in the solution is then titrated by standard sodium thiosulphate solution and starch (**279**). The amount of iodine which is found by titration will be proportional to the amount of copper which was originally present in solution, as is shown by the above equation.

In order that the result may be accurate, the copper solution must contain no free acid except acetic acid. To secure this, sodium carbonate solution is added to the copper solution until a slight permanent precipitate remains. This precipitate is then removed by the careful addition of acetic acid.

SECTION IV.

UNCLASSED VOLUMETRIC ESTIMATIONS.

Estimation of Silver by Standard Sodium Chloride Solution.

301. When solution of silver nitrate is mixed with solution of sodium chloride, the silver is precipitated as the white insoluble chloride, according to the following equation:—

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

A similar reaction occurs with any soluble silver salt; and therefore a solution of silver may be volumetrically estimated by using a solution of NaCl of suitable strength.

The most convenient method of judging the end of the reaction is to add a few drops of potassium chromate solution. Dark red silver chromate is then formed as soon as the soluble silver salt is present in excess. The method of procedure will differ according as the silver solution is neutral or acid in reaction, since potassium chromate can be used as an indicator in a neutral solution, but it cannot be employed in the presence of free acid.

302. Estimation of Silver in Neutral Solution.—If a few drops of neutral potassium chromate solution are added to the sodium chloride before the silver solution is added, the presence of the *slightest excess* of silver in solution is indicated by a permanent red colour being imparted to the turbid solution. This is due to the fact that the deep red

chromate of silver is formed when the silver solution is added in greater quantity than is necessary to precipitate all the chloride. Hence the chromate serves to indicate the end of the reaction.

Process of Estimation.—Prepare a deci-normal solution of NaCl, by dissolving $\frac{58{\cdot}51}{10} = 5{\cdot}851$ grams of NaCl in water, and diluting the solution to 1 litre.

Measure 10 c.c. of the above solution into a porcelain dish. Add three drops of neutral potassium chromate solution, and then add the silver solution from a burette, with constant stirring. As soon as a distinct permanent red tint appears the titration is complete.

In order to assist the eye in detecting the first appearance of a slight red tint in the liquid, a second similar dish containing sodium chloride solution and the chromate, to which the silver solution has been added but not in excess, should stand beside the first. The least change of colour in the liquid is then easily seen by comparing the colour of the contents of the two dishes.

Each c.c. of the NaCl solution corresponds to 0·010794 gram of silver, hence the amount of silver is easily calculated.

303. Estimation of Silver in Acid Solution.—Since silver chromate cannot be precipitated from an acid solution, the precipitation of this compound cannot be used as the indication of the completion of the process of titration, when silver is to be estimated in an acid solution.

The precipitation of the whole of the silver from solution is, however, readily known to have taken place when no further turbidity is formed on the addition of a soluble chloride. This method of judging the end of the reaction is possible, since silver chloride is insoluble in solutions containing a little free nitric acid, and it quickly subsides, leaving a clear supernatant liquid when the solution is vigorously shaken.

Deci-normal sodium chloride solution is usually employed for this estimation. It is added to the silver solution, which has been acidified with nitric acid, and the liquid is vigorously shaken. Towards the end of the precipitation, the sodium chloride is added drop by drop until no further precipitate appears on the addition of the last drop. In cases where great accuracy is required, centi-normal sodium chloride solution may be used towards the end of the process.

Process of Estimation.—Weigh out accurately about 0·4 gram of pure recrystallised silver nitrate into a well-stoppered 7-oz. bottle. Add about 100 c.c. of water, and a few drops of strong nitric acid. Cover the bottle during the titration with black velvet or cloth to prevent access of light. Then add nearly the total requisite quantity of deci-normal sodium chloride solution, about 25 c.c., and shake the bottle vigorously until the silver chloride precipitate is clotted together. Tap the bottle on the bench to cause any floating precipitate to subside.

Now drop in a little more sodium chloride solution. If the clear supernatant liquid becomes turbid, add more sodium chloride solution cautiously, taking care to shake the bottle well after each addition. This procedure is continued until no further turbidity appears.

When the point of complete precipitation is nearly reached, the precipitate will be found to subside slowly: but as soon as a drop of sodium chloride is added in excess the liquid clears almost instantaneously.

Since each c.c. of the deci-normal sodium chloride solution corresponds to 0·010794 gram of silver, the percentage of silver in the salt is readily calculated.

Estimation of Chloride in Solution by Standard Silver Nitrate.

304. The processes for the estimation of silver by standard sodium chloride solution (**302, 303**) also serve for the estima-

tion of a chloride in solution by standard silver nitrate solution.

The amount of chloride in solution may be readily estimated by adding a few drops of potassium chromate to serve as an indicator and then titrating with deci-normal silver nitrate solution.

Deci-normal silver nitrate solution is made by dissolving 16·998 grams of $AgNO_3$ in a litre of water: and each c.c. of this solution corresponds to 0·003545 gram of Cl.

If the solution of chloride contains free acid, it may be exactly neutralised by means of pure sodium hydrate solution, and may then be titrated after the addition of chromate (302). Or the neutralisation and the indicator may be dispensed with, and the chloride solution may be added from a burette to a measured volume of the standard $AgNO_3$ solution; the procedure being similar to that already described (303).

Estimation of Cyanide by means of Standard Silver Nitrate Solution.

305. The hydrocyanic acid, or soluble cyanide, is rendered alkaline by the addition of potassium hydrate solution in excess, and standard solution of silver nitrate is added. As soon as the silver solution is in excess, a precipitate of silver cyanide is formed.

A soluble double cyanide of silver and potassium is first produced in this reaction, and therefore no precipitate is formed:—

$$2KCN + AgNO_3 = KCN.AgCN + KNO_3.$$

But as soon as the silver solution is in excess, a precipitate of silver cyanide forms, and serves to indicate the end of the above reaction:—

$$KCN.AgCN + AgNO_3 = 2AgCN + KNO_3.$$

Instead of relying on the appearance of the silver cyanide precipitate, a few drops of sodium chloride solution may be mixed with the cyanide solution. The first drop of silver solution, which is added in excess of that required by the first reaction, will then produce a precipitate of silver chloride. Hence a solution of sodium chloride may be used as the *indicator*.

At the conclusion of the first stage of the reaction, each c.c. of deci-normal $AgNO_3$ solution which has been added will correspond to 0·013036 gram of KCN.

The solution to be estimated should be largely diluted with water before it is titrated.

If hydrocyanic acid in solution is to be estimated by this process, the liquid should be quickly mixed with excess of potassium hydrate solution in a beaker, else loss of volatile HCN may occur. The amount of potassium hydrate solution should correspond as nearly as possible to that necessary for converting the acid into KCN.

To prevent the inhalation of poisonous vapour, the solution of hydrocyanic acid should be weighed instead of being measured. If it is measured in a pipette, a plug of cotton-wool moistened with silver nitrate solution should be inserted into the upper end of the pipette which is used for measuring the liquid.

For practice in the estimation use commercial potassium cyanide. Weigh accurately about 1 gram of the solid cyanide; dissolve it in 250 c.c. of cold water, and use 25 c.c. of this solution for the titration. No potassium hydrate solution need be added to this solution, since the commercial salt is always alkaline. Add deci-normal $AgNO_3$ solution until a very slight permanent precipitate appears.

Estimation of Copper in Solution by means of Potassium Cyanide Solution.

306. When an ammoniacal solution of copper is brought into contact with a solution of potassium cyanide, it is

decolorised. On this fact, a process for the volumetric determination of copper in solution is based.

Since the reaction is influenced by the quantities of copper, of free ammonia and of ammonium salts which are present, care must be taken that the amounts of these substances in the solution shall be the same in every estimation.

A standard solution of a copper salt is first prepared by dissolving 5 grams of pure electrolytic copper in moderately strong nitric acid. The solution is evaporated to dryness on the water-bath to expel the excess of acid. The residue of copper nitrate is then dissolved in water, and the solution is made up to 1 litre.

A moderately strong solution of potassium cyanide is then poured into a burette. 20 c.c. of the copper solution, which correspond to 0·1 gram of Cu, are measured into a beaker, and 10 c.c. of ammonium hydrate solution of 0·9 specific gravity are added. The potassium cyanide solution is then added to the copper solution, until the full blue colour disappears, and only a *very pale lavender tint* remains. The end of the reaction is marked with greater precision by the appearance of this tint than by the total removal of the colour.

When the value of the potassium cyanide solution has been thus determined, it should be diluted until 20 c.c. correspond to 20 c.c. of the copper solution. Each c.c. of the potassium cyanide solution is then equivalent to 0·005 gram of copper.

For practice in this method, weigh out accurately about 10 grams of pure crystallised copper sulphate, $CuSO_4.5H_2O$. Dissolve this, and make up the solution to half a litre with water. Take out 20 c.c. for the titration. Add to this 10 c.c. of ammonium hydrate solution of 0·9 specific gravity; and add the potassium cyanide solution from the burette, as is described above.

From the volume of the standard potassium cyanide solution which is required, the weight of copper and the percentage present in the substance are readily calculated.

Estimation of Zinc in Solution by means of Solution of Sodium Sulphide.

307. When an ammoniacal solution of a zinc compound is treated with sodium sulphide solution, the zinc is precipitated as sulphide, $ZnSO_4 + Na_2S = ZnS + Na_2SO_4$. As soon as the least excess of sodium sulphide has been added, it is readily detected by the brown precipitate which is formed with an alkaline solution of lead. The following solutions are required.

Sodium Sulphide Solution.—Hydrogen sulphide is passed into a moderately strong solution of sodium hydrate, until the liquid smells strongly of the gas. Sodium hydrate solution is then added in quantity sufficient to remove the odour of the gas. This solution is suitably diluted, and is used for the titration.

Alkaline Solution of Lead.—Lead acetate solution is heated with a mixture of tartaric acid solution and excess of sodium hydrate. Neutral sodium tartrate solution may be substituted for the mixture of tartaric acid with sodium hydrate. As soon as the lead solution becomes clear, the heating is stopped, and the liquid is ready for use.

Standard Solution of Zinc Sulphate, containing 10 grams of Zn per litre. This is prepared in one of the two following ways:—

(1). Dissolve 10 grams of pure zinc in the least possible quantity of dilute sulphuric acid, and dilute this solution to 1 litre.

(2). Dissolve 43·9 grams of pure $ZnSO_4.7H_2O$ in water, and dilute the solution to 1 litre.

The Process of Titration.—Transfer 25 c.c. of the zinc solution to a beaker. Then mix a little ammonium carbonate solution (1 : 5) with three times its volume of ammonium hydrate solution (1 : 3). Add this reagent to the zinc

solution until the precipitate, which forms at first, is just redissolved.

Space out separately at intervals with a glass rod a few drops of the alkaline lead solution upon a piece of filter-paper which is placed upon a white tile.

Now add the solution of sodium sulphide to the zinc solution with constant stirring. From time to time place a drop of the liquid by means of a glass rod upon the filter-paper, sufficiently close to a drop of the lead solution to expand and join it. In this way the ZnS precipitate is filtered off, and the liquid in which it was suspended alone comes into contact with the lead solution. It must be remembered that the lead solution is blackened by contact with the moist ZnS.

As soon as a dark line appears at the point of contact of the drops, the precipitation of the Zn is complete. After a little practice, the end of the reaction may be judged with great precision.

The sodium sulphide solution, which has been prepared as is directed above, will probably be shown by this titration to be too strong. It must be diluted, if necessary, until from 15 to 20 c.c. of the solution are required to precipitate 25 c.c. of the zinc solution.

When zinc is to be estimated by this method in a solution, an aliquot part of the solution is rendered ammoniacal, as has been already described; it is then titrated with the sodium sulphide solution in the manner just stated.

Estimation of P_2O_5 in Soluble Phosphates by means of Uranium Solution.

308. This process depends upon the fact, that when solution of uranium nitrate or of uranium acetate is added to solution of a phosphate, in the presence of an alkaline acetate and free acetic acid, the whole of the phosphate is thrown down as uranium phosphate.

The uranium solution is usually added to the solution of the phosphate. The presence of an excess of uranium solution is detected by the formation of a brown precipitate of uranium ferrocyanide, when a drop of the liquid is brought into contact with a drop of freshly-prepared potassium ferrocyanide solution.

The following solutions are required :—

Standard Solution of Uranium Nitrate. — Weigh out roughly 35 grams of uranium nitrate, or the chemically equivalent weight of uranium acetate, add 25 c.c. of glacial acetic acid, dissolve the salt, and dilute the solution to a litre with water.

Standard Sodium Phosphate Solution.—Weigh out accurately 10·085 grams of the pure, recrystallised, non-effloresced salt. Dissolve this in water and dilute the solution to a litre. 50 c.c. of this solution correspond to 0·1 gram of P_2O_5.

A Solution of Sodium Acetate containing Acetic Acid.— This solution is prepared by dissolving 100 grams of sodium acetate in water, adding 100 c.c. of acetic acid of about 1·04 specific gravity, and diluting the liquid to a litre.

A Solution of Potassium Ferrocyanide, which must be freshly prepared.

309. *The Process of Titration.*—Add to 50 c.c. of the sodium phosphate solution 5 c.c. of the sodium acetate solution, and heat the liquid to 90° C. Now add the uranium solution from a burette, until a drop of the liquid, when it is brought into contact with a drop of potassium ferrocyanide solution, gives a faint reddish-brown coloration.

Heat the liquid once more to 90° C., and test a drop again with ferrocyanide. If the brown coloration still appears, the titration is completed. If, however, no coloration appears, continue to add the uranium solution, until the brown colour

is produced with the ferrocyanide after the liquid has stood for some time.

The uranium solution must now be diluted until 50 c.c. of the phosphate solution require 20 c.c. of the uranium solution. Each c.c. of the uranium solution will then correspond to 0·005 gram of P_2O_5.

In the final titration it is best to add nearly the whole of the uranium solution *rapidly*, and to finish the titration by *cautiously* adding the remainder.

The above procedure indicates the method of estimation of phosphate in aqueous solution.

A special method of titration of the uranium solution, however, is necessary when the solution is to be used for the estimation of calcium phosphate or magnesium phosphate in acid solution (**310**).

310. Estimation of Calcium and Magnesium Phosphates.—These phosphates cannot be correctly estimated by uranium solution, which has been standardised by means of sodium phosphate solution. The uranium solution, which is used for the estimation of P_2O_5 in either of these phosphates, must be standardised by a solution which contains 5 grams per litre of tricalcium phosphate instead of by the sodium phosphate solution.

Before this solution is prepared the purity of the tricalcium phosphate must be tested as follows:—Weigh out accurately about 0·5 gram of pure commercial calcium phosphate. Dissolve this in a small quantity of nitric acid. Add a large excess of ammonium molybdate solution (**449**), and allow the liquid to stand in a warm place for several hours. The process of precipitation must be proved to be complete by warming some of the clear liquid with more molybdate solution. Dissolve the precipitate thus produced in ammonium hydrate solution, and estimate the P_2O_5 as $Mg_2P_2O_7$ (**131**). From this result, the amount of pure $Ca_3(PO_4)_2$ in the commercial phosphate can be calculated.

Now weigh out a quantity of the commercial phosphate,

which contains 5 grams of pure $Ca_3(P_4O_4)_2$. Dissolve this in a slight excess of dilute HCl, and dilute the solution to a litre. Measure 50 c.c. of this solution into a beaker, mix this with 5 c.c. of the sodium acetate solution, and add the uranium solution to the *cold liquid*, until the final point is nearly reached; then heat to 90° C. and complete the titration (309).

Note.—If the phosphate solution is heated at the beginning of the titration, calcium or magnesium phosphate may precipitate, and is then redissolved in acetic acid only with much difficulty.

From the result of this titration the phosphate-value of the uranium solution, when it is applied to the estimation of calcium or magnesium phosphate, is determined.

311. Estimation of Phosphates of Unknown Composition. — A substance of unknown composition, in which phosphate is to be estimated by standard uranium solution, must first be subjected to qualitative analysis. The conditions specified in paragraphs 309, 310 with respect to the process of titration must then be observed.

PART IV.

GENERAL QUANTITATIVE ANALYSES.

Introductory.—The student who has worked according to the directions given in the preceding pages will have gained experience in many ordinary processes of simple gravimetric and volumetric analysis, and will be in a position to understand and perform some more complicated analyses.

A series of analyses are accordingly described in this part of the book, many of which involve quantitative separations. The processes which are made use of are either gravimetric or volumetric; that process being always selected which is most suitable to each analysis. Most of the processes which are described are those actually in use for technical, manufacturing, and agricultural purposes; others serve for the examination of articles of food and drink. Most of these analytical processes are also suitable for determinations required for scientific purposes, and those described under Organic Analysis, in Section IV., are almost entirely thus employed.

329. Books of Reference.—The following books may be consulted, in addition to those which have been already mentioned, for further special and technical information on analyses similar to those which are described in this part of the book :—

Allen's Commercial Organic Analysis;
Hassall's Food Analysis;
Crookes' Select Methods of Analysis;

Lunge's Sulphuric Acid and Alkali;
Wanklyn's Milk Analysis;
Hehner's Butter Analysis;
Frankland's Water Analysis;
Wanklyn's Water Analysis;
Addyman's Agricultural Analysis;
Classen's Application of Electrolysis to Chemical Analysis;
Watts' Dictionary of Chemistry;
Thorpe's Dictionary of Applied Chemistry;
Beringer's Manual of Assaying.

New methods of analysis will also be found described from time to time in the *Journals of the Chemical Society*, and of the *Society of Chemical Industry*, and in the *Chemical News* and the *Analyst*.

SECTION I.

ANALYSIS OF ALLOYS, ORES, MINERALS, IRON AND STEEL, COAL, &c.

Estimation of Silver and Copper in a Silver Coin.

Two methods of estimation are here described, one of which is volumetric, and the other is gravimetric.

330. Volumetric Method.—Weigh accurately a sixpenny-piece, or about 2 grams of clippings or turnings obtained from a silver-alloy. Introduce the alloy into a small flask, and place a small funnel in the neck of the flask. Pour a few c.c. of strong nitric acid and a little water through the funnel into the flask. A violent reaction will ensue. As soon as this ceases, heat the flask on the water-bath, adding a little more nitric acid, if necessary, to complete the solution of the metal.

Now heat the solution in an evaporating dish on the water-bath, until most of the free acid has been expelled. Then add water and make up the solution to 200 c.c. with distilled water.

Estimation of the Silver.—Measure 20 c.c. of this solution into a well-stoppered bottle, and add deci-normal sodium chloride solution gradually from a burette, shaking the liquid in the bottle vigorously. The solution must be added until no further precipitate is produced in the clear liquid in the bottle by the addition of the last drop of the sodium chloride solution (**303**).

Each c.c. of the sodium chloride solution corresponds to

0·010794 grams of silver, hence the percentage weight of silver in the coin is readily calculated from the result of the titration.

Estimation of the Copper.—Measure 50 c.c. of the above solution of the alloy into a beaker, add excess of sodium chloride solution, and filter off and wash the silver chloride precipitate. Add to the filtrate and washings 20 c.c. of ammonium hydrate solution of 0·93 specific gravity, and titrate the liquid with standard potassium cyanide solution (**306**).

An alternative method for estimating the copper is that effected by means of potassium iodide and sodium thiosulphate solution (**300**).

331. Gravimetric Method. — Weigh accurately half a threepenny-piece, or about 0·5 gram of the clippings or turnings from the silver-alloy. Dissolve this in nitric acid, and expel most of the free acid by evaporation.

Estimation of the Silver.—Add to this solution an excess of sodium chloride solution. Boil the liquid, and filter off, wash, and weigh the precipitated silver chloride (**123**).

Estimation of the Copper.—Heat the filtrate and washings from the silver chloride to boiling, and add a slight excess of potassium hydrate solution. Then filter off and weigh the copper oxide thus precipitated (**90**).

The thiocyanate method of estimation (**338**) may be substituted with advantage for the above method.

Valuation of Zinc-ores.

332. The volumetric process (**307**) is convenient for estimating the percentage of zinc in many of its ores.

Blende and other zinc-ores often contain lead, copper, and cadmium. These metals must be removed from the solution by precipitation with hydrogen sulphide before the zinc is estimated. Iron and manganese also interfere with the accuracy of the titration; they may be removed as is de-

scribed below. A preliminary qualitative analysis of the zinc-ore should always be made to ascertain whether any of these metals are present.

333. Estimation of the Moisture.—It is advisable in all cases to estimate the amount of moisture in the ore, since this renders it possible to calculate the percentage of zinc in the dry ore.

For this purpose weigh out accurately from 1 to 2 grams of the finely-powdered ore. For rich ores 1 gram, and for the poorer ores 2 grams, will be found a suitable quantity for analysis. Heat the ore in the steam-oven, until its weight becomes constant (152). The loss of weight which it suffers gives the amount of moisture.

334. Estimation of the Zinc.—Place the dried ore (333) in an 8-oz. beaker, and add a little aqua-regia. Heat until solution is complete, and remove the excess of acid by heating the liquid in an evaporating dish.

If lead is present, add a few drops of strong sulphuric acid, and evaporate until dense white fumes appear. Extract the residue with water, and filter. If any other metals of the hydrogen sulphide group be present, such as copper, they must be precipitated by passing hydrogen sulphide.

If the solution contains iron and manganese, convert the iron into the ferric condition by heating the solution or the filtrate with a little strong nitric acid. Add bromine-water in excess to the cold solution, then ammonium hydrate in slight excess, and boil. Filter off the precipitate, which consists mainly of ferric hydrate, and wash it until the washing-water is free from zinc, as is shown by adding Am_2S to a few drops of the washings. Add the washings to the filtrate.

If the iron precipitate is large in amount, it must be dissolved in hydrochloric acid, and then reprecipitated and washed as before. This procedure will dissolve out the zinc which is invariably precipitated with the iron. The second filtrate and washings are added to those previously obtained.

Make up this ammoniacal zinc solution to 1 litre. Add to 50 c.c. of the solution standard sodium sulphide solution from a burette, until a drop of the liquid, taken out by means of a glass rod, gives a dark line of contact when it is allowed to expand and meet a drop of alkaline lead acetate solution which has been absorbed by a piece of filter-paper (307).

It is necessary to titrate the standard sodium sulphide solution before it is used, since it undergoes change by keeping.

Valuation of Copper-ores.

Four methods of estimating the amount of copper in the solution of a copper-ore are described below. The first is an electrolytic method (335). The second is the Mansfeld method (336), and is an application of the cyanide process (306). The third is commonly known as the iodide method (337). The fourth is the thiocyanate method (338).

335. **The Electrolytic Method.**—In this process the copper is precipitated from the solution of the ore by a galvanic current, and is then weighed in the metallic state.

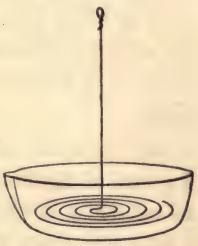
Preparation of the Solution of the Ore.—For the estimation weigh accurately about 2 grams of the finely-powdered sample: and if it contains bituminous matter, oxidise and expel the organic matter by ignition in the air.

Then proceed to dissolve the copper as follows. Pour a little moderately dilute nitric acid upon the ore in an evaporating dish, and add about the same quantity of dilute sulphuric acid. Cover the dish with an inverted funnel, and evaporate nearly to dryness on a sand-bath in order to expel the excess of nitric acid. Dissolve the residue in water, adding a few drops of nitric acid if necessary, and filter.

Electrolysis of the Solution.—Now transfer the clear liquid to a weighed platinum dish, placed upon a bright metal ring of a retort stand. Twist a stout platinum wire into a flat

spiral, leaving about 6 inches in the centre projecting at right angles to the plane of the spiral (fig. 73). Attach the spiral to a glass rod, which is clamped upon the retort stand: and immerse it in the solution, taking care that there is no metallic contact between the platinum wire and the dish. The spiral should be arranged about the eighth of an inch from the bottom of the dish.

Fig. 73.



Instead of the spiral, a disc of thick platinum-foil, riveted to a long stout platinum wire, may be used.

The dish is now connected with the zinc plate of a battery of two Daniell's cells, or their equivalent. This is readily done, since the dish is in metallic connection with the retort stand; it is therefore simply necessary to attach the battery-wire to the ring or to the stand, taking care that the surfaces in contact are bright and metallic. The platinum spiral or disc is then connected with the copper plate of the battery.

After some hours the copper will be completely precipitated, and will adhere to the inside of the platinum dish.

During the deposition of the metal, the dish must be covered by a perforated clock-glass, or by a sheet of mica. This prevents the loss of any liquid by the spirting which is caused by the evolution of gas from the surface of the spiral. The under surface of the cover should be rinsed into the dish during the latter part of the process.

Weighing the Copper.—As soon as a few drops of the liquid from the dish give no coloration with H_2S solution, the dish is rinsed out first with water, and finally with a few drops of alcohol. It is then dried in the steam-oven and weighed. From the increase of weight of the dish, the percentage of copper present in the ore is calculated.

The copper may be removed from the dish by dissolving it in nitric acid.

This process of estimation requires no supervision after it

has been started, and it can therefore be allowed to proceed during the night.

336. The Mansfeld Method.—The ore is first dissolved in acid, and the whole of the copper is precipitated from this solution by immersing in it a piece of zinc and a strip of platinum-foil. The copper is then dissolved from the platinum strip by nitric acid. The acid solution is rendered alkaline by the addition of ammonium hydrate in excess, and the alkaline solution is titrated with standard potassium cyanide solution (306).

(a). *Solution of the Copper.*—Weigh accurately about 5 grams of the finely-powdered ore into a 10-oz. flask. Add 40 c.c. of hydrochloric acid of 1·16 specific gravity. After a time add 6 c.c. of dilute nitric acid, made by mixing equal measures of water and of nitric acid of 1·2 specific gravity. Gently heat the flask for 30 minutes on a sand-bath, and finally boil the liquid for 15 minutes. The whole of the copper will now be in solution. Remove the insoluble residue by filtration, receiving the filtrate in an 18-oz. beaker.

(b). *Precipitation of the Metallic Copper.*—A zinc rod, free from lead, and weighing about 50 grams, is attached to a piece of platinum-foil. This is placed in the filtrate containing the copper. The precipitation of the copper in the metallic state commences as soon as the warm filtrate comes into contact with the zinc and platinum, and is complete in about half an hour. The spongy copper partly adheres to the platinum, and is partly suspended in the liquid. Remove the zinc and platinum, and wash the precipitated copper repeatedly by decantation.

(c). *Titration of the Standard Cyanide Solution.*—Standard potassium cyanide solution must now be prepared as follows. Weigh into a litre-flask exactly 5 grams of chemically pure copper, which has been preferably deposited electrolytically. Dissolve this in 266·6 c.c. of nitric acid, consisting of equal measures of water and of nitric acid of 1·2 specific gravity. Dilute this solution to 1 litre.

Pour 30 c.c. of this copper solution, which is equivalent to 0·15 gram of metallic copper, into a small beaker. Add 10 c.c. of dilute ammonium hydrate solution, made by mixing one volume of ammonium hydrate of 0·93 specific gravity with two volumes of water. Then add the potassium cyanide solution from a burette to this solution, until its blue colour fades to a *very pale* lavender (**306**).

The copper-value of the potassium cyanide solution is thus determined, and the strength of the solution must be so adjusted that each c.c. is equivalent to 0·005 gram of copper.

(d). *Estimation of the Copper.*—Dissolve the copper, which was precipitated from the solution of the ore (b), in 8 c.c. of nitric acid of the strength described above (c). Add 10 c.c. of the dilute ammonium hydrate solution (c), and proceed with the titration as is described above (c).

If the amount of copper in the ore exceeds 6 per cent., dissolve the precipitated copper in 16 c.c. of the dilute nitric acid, make up the solution to 100 c.c. with distilled water, and withdraw 50 c.c. for the titration.

The calculation of the percentage weight of copper in the ore from the result of the titration is very simple. For, since 5 grams of the ore are used and each c.c. of the potassium cyanide solution corresponds to 0·005 gram of copper, each c.c. of the cyanide solution used in the titration represents 0·1 per cent. of copper.

This method is rapid, and is accurate if it is always carried out under the same conditions. Care must, however, be taken that lead is not present in large quantity. Zinc must be entirely absent. The solution should be cold, as a higher temperature seriously interferes with the titration. The strength of the copper solution to be titrated should not vary greatly; and finally the same amount of ammoniacal salt should be present in each determination.

337. Iodide Method.—Weigh accurately about 2 grams of the finely-powdered ore, and prepare the copper solution

as is directed under the electrolytic method (335). Precipitate the copper completely from the diluted solution by passing hydrogen sulphide. Filter, and wash the precipitate with water containing hydrogen sulphide.

Dissolve the precipitate by heating it with a small quantity of nitric acid, evaporate nearly to dryness, add some water, and boil the liquid until it ceases to evolve nitrous fumes. Add sodium carbonate until a small permanent precipitate is formed, then add acetic acid in slight excess. Dilute this liquid to 200 c.c., and estimate the copper by adding potassium iodide solution in excess, and titrating the iodine by standard sodium thiosulphate solution (300).

338. Estimation of Copper as Cuprous Thiocyanate.—The copper ore is treated as is directed in par. 335 to prepare a solution of the copper. For this estimation, however, the copper solution must not contain free nitric acid. Hence the free acid in the solution is neutralised by adding ammonium hydrate solution in slight excess. The liquid is then rendered faintly acid in reaction by the addition of dilute HCl.

The copper is then completely precipitated from the solution by adding an excess of a solution of equal weights of ammonium thiocyanate and of ammonium bisulphite. The liquid is poured through a tared filter-paper, and the white precipitate of copper thiocyanate, $Cu_2(CNS)_2$, is washed, and then dried in the steam-oven until its weight is constant.

Note.—Since copper is the only metal which is thus precipitated as thiocyanate in a solution of chlorides acidified with HCl, the above process serves to separate Cu from all other metals in such a solution.

Valuation of Soda-ash.

339. Soda-ash consists essentially of anhydrous sodium carbonate, but it always contains a certain proportion of sodium hydrate, besides other substances.

Moisture, sodium carbonate, and sodium hydrate are commonly estimated in soda-ash.

340. Estimation of Moisture.—Weigh 10 grams of the powdered soda-ash into a platinum crucible. Heat the covered crucible for about half an hour over a small Bunsen-flame, and weigh it when it is cold. The loss of weight gives the moisture contained in the sample.

341. Estimation of Sodium Carbonate and Sodium Hydrate.—Transfer the dried salt (**340**) to a beaker and dissolve it in water. Filter, and wash any insoluble matter; then dilute the filtrate and washings to 500 c.c. and mix the liquid well by shaking.

Mix 50 c.c. of this solution with a few drops of phenol-phthalein solution (**228**). Then add normal sulphuric acid (**236**) slowly until the red colour of the liquid is just destroyed.

At this point *all* the sodium hydrate and *one-half* of the sodium carbonate will have been neutralised. For, since phenol-phthalein is sensitive to free carbonic acid, its red colour will disappear as soon as the whole of the sodium carbonate is converted into bicarbonate, and a trace of the carbonic acid which is liberated by the acid remains uncombined.

Now add a few drops of methyl-orange solution (**227**), and continue to add the standard acid until the colour of the solution changes from yellow to pink. At this stage the whole of the bicarbonate will be neutralised.

It will be seen that the sodium, which was present as carbonate in the original solution of the soda-ash, is equivalent to twice the quantity of acid which was required for neutralisation after the addition of the methyl-orange. Also that the amount of sodium hydrate in the original solution is equivalent to the total amount of acid used, less that corresponding to the carbonate.

The following illustration will render the procedure and the method of calculation intelligible.

Example.—In a particular estimation, 10·024 grams of soda-ash were dissolved in water, and the solution was made up to 500 c.c.

This liquid was titrated with normal sulphuric acid solution, each c.c. of which corresponds to 0·05306 gram Na_2CO_3, and to 0·04006 gram NaHO.

With phenol-phthalein as an indicator, 50 c.c. of this solution required 9·6 c.c. of normal sulphuric acid.

On the addition of methyl-orange, 8·4 c.c. of additional acid were required.

Therefore the total amount of acid required was $9·6 + 8·4 = 18·0$.

Hence the amount of acid equivalent to the sodium carbonate present in 50 c.c. of this solution was $= 8·4 \times 2 = 16·8$ c.c.

And 500 c.c. would require $= 16·8 \times 10 = 168$ c.c. of acid.

Therefore the amount of Na_2CO_3 in 10·024 grams of the soda-ash $= 168 \times 0·05306 = 8·9141$ grams.

Hence the percentage of $Na_2CO_3 = \frac{8·9141 \times 100}{10·024} = \underline{88·93}$.

The amount of acid equivalent to the sodium hydrate in 50 c.c. of the solution is $18 - 16·8 = 1·2$; hence the acid equivalent to 500 c.c. $= 1·2 \times 10 = 12$ c.c.

Therefore the amount of NaHO in 10·024 grams of the soda-ash is $12 \times 0·04006 = 0·48072$.

Hence the percentage of $NaHO = \frac{0·48072 \times 100}{10·024} = \underline{4·85}$.

Note.—In technical analyses it is usual to state the weights of Na_2O which are present as carbonate and as hydrate.

Valuation of Manganese-ores.

342. The value of a manganese-ore for the preparation of chlorine, and for other purposes, depends upon the amount of "available oxygen" which it contains. The "available oxygen" is that part of the oxygen which becomes available for oxidation when the oxide is dissolved by an acid. It will be seen from the following equation that this amounts to half the oxygen in MnO_2:—$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$.

Three methods for estimating the commercial value of manganese-ore are described below. If the valuation is required for technical purposes, the methods described in pars. **344**, **345** are most suitable, since they determine the

amount of oxygen actually available in practice. The methods described in **346**, **347**, however, indicate the amount of manganese peroxide present with greater accuracy.

Many samples of manganese-ore contain ferrous oxide. This reduces the actual amount of oxygen available in the manganese oxide, since the ferrous oxide is oxidised to ferric oxide, and appropriates some of the oxygen during the applications of the manganese oxide.

When the estimation is to be made, about 10 grams of the oxide are finely powdered (**34**, **35**) as rapidly as possible, and the powder is placed in a stoppered weighing-bottle.

343. Estimation of Moisture.—Most manganese-ores contain combined water, in addition to hygroscopic moisture. The latter alone is usually estimated.

Weigh out from 2 to 4 grams of the ore accurately in the watch-glasses and clamp (**16**), and heat it in the air-oven (**350**) to 120° C. until the weight becomes constant. This temperature drives off the hygroscopic moisture only.

344. Indirect Estimation of the Available Oxygen by KI and Thiosulphate.

Bunsen's Method.—Weigh accurately about 0·5 gram of the finely-powdered dried ore (**343**) into the small flask (*a*), (fig. 72, **295**), and warm it with about 25 c.c. of strong hydrochloric acid. The chlorine, which is given off, is absorbed in potassium iodide solution contained in the U-tube. The chlorine liberates its chemically equivalent quantity of iodine, which is then titrated with standard sodium thiosulphate solution (**296**).

The available oxygen is usually calculated in terms of manganese dioxide, according to the equation, $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$.

345. Estimation of the Available Oxygen by the Oxidation of a Ferrous Salt.—Weigh accurately from 1 to 2 grams of pianoforte-wire, and dissolve it in dilute

sulphuric acid as is described in paragraph **255**. Then weigh accurately about 1·5 grams of the dry finely-powdered manganese-ore (**343**), and add it to the iron solution. Heat the solution until the ore is dissolved, carefully avoiding the access of air.

As soon as the solution of the ore is complete, the amount of unaltered ferrous salt is estimated by means of standard potassium permanganate (**264**) or by standard potassium dichromate solution (**255**).

The available oxygen is usually calculated from this result in terms of manganese dioxide, from the equation,

$$2FeSO_4 + MnO_2 + 2H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O.$$

346. Estimation of the Available Oxygen by the Oxidation of Oxalic Acid.—Reference to paragraph **150** will indicate another method of valuing manganese-ore, which may be applied either gravimetrically or volumetrically.

The weight of oxalic acid which can be oxidised by the manganese oxide is thus obtained. 90 parts of $H_2C_2O_4$ correspond to 87·05 parts of manganese dioxide: and from this relation the weight of MnO_2 may be calculated.

Gravimetric Estimation.—Weigh out accurately about 3 grams of the finely-powdered manganese ore (*Note*, **150**). Introduce this, together with $2\frac{1}{2}$ times its weight of neutral potassium oxalate, into the decomposition flask (**140**, **147**, **148**). Allow strong sulphuric acid to flow in, and estimate the CO_2 which is evolved as is directed in the above paragraphs.

Volumetric Estimation.—Pour upon 2 grams of the ore, contained in a flask, 50 c.c. of normal oxalic acid solution and 5 or 6 c.c. of strong sulphuric acid. Heat the mixture until all black grains have disappeared. Then filter the liquid, and make the filtrate up to 250 c.c. Determine the amount of undecomposed oxalic acid in this solution by titrating it with standard permanganate solution (**266**).

Estimation of the Amount of Hydrochloric Acid required to decompose a Manganese-ore.

347. It is sometimes necessary to determine for technical purposes the amount of hydrochloric acid which is necessary to decompose a manganese-ore.

The amount of manganese peroxide found in a manganese-ore does not give a true indication of the amount of hydrochloric acid necessary for its decomposition, since in many manganese-ores, Mn_3O_4, earthy carbonates and iron compounds are present. Hence the amount of free acid which disappears during the solution of the manganese-ore, is usually in considerable excess of the amount actually decomposed by the MnO_2.

348. For the estimation of the amount of acid actually required by the ore, use hydrochloric acid of about 1·12 specific gravity. First ascertain the strength of the acid by means of normal sodium hydrate solution (**239**). Then pour 1 gram of the finely-powdered ore (**34, 35**) into a small flask, add 10 c.c. of hydrochloric acid of the above gravity, connect the flask with an inverted Liebig's condenser, and heat the acid until all action ceases.

Now add to the cool residual acid liquid standard sodium hydrate solution from a burette, until the reddish-brown precipitate of ferric hydrate, which first appears, does not redissolve when the liquid is well shaken. This will measure the excess of acid left after the decomposition of the manganese-ore.

The amount of acid required for the decomposition of the ore is that which is found to have disappeared during the process of heating.

Since the amount of chlorine which has been evolved during the action of the acid may be obtained (**344**), the quantity of chlorine remaining combined as chloride in solution can be calculated by difference.

Analysis of Limestone and of Magnesian Limestone.

349. Limestone consists essentially of varying proportions of calcium and magnesium carbonates. If the proportion of magnesium carbonate is large, the limestone is called

magnesian limestone or dolomite. Limestone also usually contains moisture, silicious matter, iron, and aluminium; and occasionally manganese, alkali-metals, and carbonaceous matter. Since the constituents of limestone may vary, an exhaustive qualitative examination should precede the quantitative analysis of the limestone.

For practice in the following method of quantitative analysis, select a homogeneous piece of dolomite. Reduce about 10 grams of the substance to fine powder (34, 35), and place the powder at once in a stoppered weighing-bottle.

350. Estimation of Moisture.—Dolomite rarely contains much moisture. In order to ascertain whether any moisture is present, and at the same time to estimate its amount, weigh out accurately from 1·5 to 2 grams of the powder in the watch-glasses and clip (16), remove the clip and upper glass, and heat the lower glass and powder in the air-oven (40) for an hour, at a temperature of about 200° C.

Then remove the substance from the air-oven, immediately covering it with the other glass; replace the clip, and allow the glasses to cool in the desiccator. Weigh the glasses when they are cold. If any loss of weight has occurred, heat again in the same way in the air-oven for half an hour, and weigh once more. Repeat these processes until the weight remains constant in two successive trials. The loss of weight thus found gives the amount of moisture present.

351. Estimation of Carbon Dioxide.—Transfer the dried dolomite (350) to a flask (*a*) shown on page 117. Decompose the carbonate with hydrochloric acid, and estimate the CO_2 gas which is evolved exactly as is described in paragraph 140.

Care should be taken that the soda-lime absorption-tube (*f*) is of sufficient capacity to completely absorb the CO_2 gas: or, better still, a second somewhat smaller soda-lime tube should be attached to (*f*). Any increase of weight of this second tube is then added on the gain of weight of the

tube (f). This second tube, or "guard tube," not only serves to insure complete absorption of the CO_2, but it also indicates when the soda-lime in (f) is becoming saturated by repeated use and requires to be renewed.

Caution.—Care must be taken to preserve without loss the solution obtained in this process, as well as all the filtrates and washing-waters obtained in the subsequent processes, since these liquids are employed in the processes of estimation.

352. Estimation of Silicious Matter.—The insoluble residue which is left in the flask (**351**) consists of sand and clay. A small quantity of silica will probably also have passed into the acid solution. The whole of the silica present in the limestone is usually estimated in one weighing as follows.

The contents of the flask are carefully rinsed out into a porcelain dish 4 inches in diameter, a little strong nitric acid is added, and the liquid is evaporated to dryness on the water-bath. The dish is further heated on the water-bath, until no moisture is deposited on a cold clock-glass, when it is placed upon the dish.

The dish is then allowed to cool, and its contents are heated with a little strong hydrochloric acid so as to dissolve everything except the silica and the clay. A little water is added, the liquid is filtered, and the residue in the filter is washed until it is free from acid.

The residue is then ignited. If it is small in amount, it is ignited together with the filter (**73**). If, however, the amount of residue is considerable, the filter is more conveniently incinerated apart (**74**).

The residue thus estimated consists of silica and clay.

353. Estimation of Ferric Oxide and Alumina.—Add to the filtrate and washings from the estimation of silica (**352**) a considerable quantity of ammonium chloride solution; then add ammonium hydrate in very slight excess. Heat the solution nearly to boiling, and filter.

Wash the precipitate of aluminium and iron hydroxides

twice with hot water: then dissolve it in hot dilute hydrochloric acid, and reprecipitate the iron and aluminium by adding ammonium hydrate in slight excess.

This double precipitation is necessary, in order to completely separate the small quantity of calcium, which is precipitated with the iron and aluminium in the first instance.

Filter, and wash the precipitate until it is free from dissolved chlorides. Carefully reserve the above filtrates and all the washings.

If the precipitate is small in amount, and it is not intended to estimate the iron and aluminium separately by par. **354, a**, the precipitate may now be dried in the steam-oven, and ignited at a bright red-heat in a platinum crucible. The filter and precipitate may be ignited together (**73**). The ignited residue is weighed: it will consist of Fe_2O_3 and Al_2O_3.

This residue is reserved, if necessary, for par. **354, b**.

354. Separate Estimation of Iron and of Aluminium, or of Aluminium by Difference.—If the amounts of iron and of aluminium present are to be determined, proceed to separate these metals and to estimate them separately (**a**), or to determine the aluminium by difference (**b**).

The second method (**b**) is more rapidly carried out than the first (**a**).

(**a**). *Separate Estimation of Aluminium and of Iron.*—Dissolve the washed precipitate of aluminium and iron hydroxides (**353**) upon the filter in hot dilute hydrochloric acid, and allow the solution to flow into a nickel or porcelain dish containing about 50 c.c. of strong potassium hydrate solution, which must be free from alumina. Wash out the acid, which remains adhering to the filter-paper, with a small quantity of water, and allow these washings also to run into the dish. Boil the contents of the dish for a few minutes. The iron will be precipitated as ferric hydroxide, while the aluminium hydroxide will remain in solution.

The iron precipitate is filtered off. It is again dissolved in hydrochloric acid and reprecipitated by ammonium

hydrate, in order to free the ferric hydroxide from potassium hydrate. It is then filtered off and washed, and ignited at a red heat (73), and is weighed as Fe_2O_3 (92).

The filtrate, which consists of solution of aluminium hydroxide in potassium hydrate solution, is treated with a slight excess of strong hydrochloric acid, and then with ammonium hydrate in very slight excess. The precipitate is filtered off, washed, dried, and ignited, and is weighed as Al_2O_3 (93).

(b). *Estimation of Iron, and of Aluminium by Difference.*—The weighed precipitate of Fe_2O_3 and Al_2O_3 (353) is dissolved by prolonged heating with strong HCl. The iron in the solution is reduced by means of stannous chloride (261), or by ammonium bisulphite (262), and is titrated by means of dichromate solution (256).

The weight of Fe thus found is calculated as Fe_2O_3, and this weight is subtracted from the original weight of the precipitate containing the Fe_2O_3 and Al_2O_3. The difference represents the weight of the Al_2O_3.

355. **Estimation of Manganese.**—If only a trace of manganese is present in the limestone it may be neglected, since it will be precipitated with the iron and will cause no appreciable error. If, however, there is any quantity of manganese present, the iron and aluminium must be first precipitated as basic acetates (365): and the manganese is afterwards precipitated from the filtrate as hydrated peroxide, and is estimated as is directed in paragraph 368.

356. **Estimation of Calcium.**—Mix together the ammoniacal filtrates and washings from the iron and aluminium precipitate (353), heat the liquid to boiling, and then add a moderate excess of solid ammonium oxalate (110). Filter, and wash the precipitated calcium oxalate two or three times. Redissolve the precipitate in hot dilute hydrochloric acid: and repeat the precipitation by adding a slight excess of ammonium hydrate solution, together with a few drops of ammonium oxalate solution. Filter; wash, dry, and ignite the precipitate, and weigh it as carbonate or as oxide (110, 111).

The above reprecipitation of the calcium oxalate is necessary, in order to completely separate the magnesium which accompanies the first calcium oxalate precipitate.

357. Estimation of Magnesium.—Pour the filtrates and washings from the precipitation of the calcium (**356**) into a porcelain dish 6 inches in diameter. Evaporate this liquid to dryness, lightly greasing the inside of the edge of the dish to prevent the solution from creeping over. As soon as all the liquid has been driven off, place the dish on a sand-bath or on a piece of wire-gauze, and heat it as long as fumes of ammonium salts are driven off. This removal of ammonium salts is necessary, since they prevent the complete precipitation of magnesium.

Treat the residue in the cool dish with a little strong hydrochloric acid, warm, add water, and filter if necessary. To the clear solution add ammonium hydrate in moderate excess, then add excess of sodium hydrogen phosphate solution. Allow the liquid to stand for a few hours, or shake it vigorously in a stoppered bottle. Filter, and wash the precipitate with dilute ammonium hydrate solution; then ignite it, and weigh the Mg as $Mg_2P_2O_7$ (**130**).

358. Estimation of the Alkali-Metals.—The alkali-metals, sodium and potassium, are not usually estimated in a limestone. They can be estimated, if necessary, by dissolving 5 grams of the dolomite in hydrochloric acid, then making the liquid alkaline by the addition of excess of milk of lime, and heating. The milk of lime is prepared by stirring up fresh and *pure* slaked lime into a cream with water; it precipitates all the metals except those of the alkalis.

The excess of lime is removed by first adding ammonium hydrate and ammonium carbonate solutions in excess, and then a few drops of ammonium oxalate solution. The precipitate is filtered off, and the filtrate is acidified with HCl, and evaporated to dryness in a weighed porcelain or platinum dish.

The chlorides of sodium and potassium thus obtained are

heated for a short time on the sand-bath, and are finally weighed after cooling in the desiccator.

Since a little calcium is frequently present, this residue should be dissolved in water containing a few drops of dilute HCl, and a few drops of solution of AmHO and of $Am_2C_2O_4$ should be added. If a precipitate forms, filter; evaporate the filtrate, and ignite and weigh the residue.

359. The Proportions of the Sodium and Potassium Chlorides which are present in this residue may be determined by either of the following methods.

(1) The weighed residue is dissolved in water, a few drops of HCl are added, and then an excess of platinum chloride solution. The liquid is then evaporated on the water-bath, and the residue is treated with alcohol, in which the potassium salt, K_2PtCl_6, is insoluble: it is weighed as is described in paragraph **136**. The weight of potassium chloride present is then calculated, and the weight of the sodium chloride can be found by difference.

(2) The weighed residue is dissolved in water, and the weight of chlorine present in the chlorides is determined by titration with standard silver nitrate solution (**304**).

The weights of sodium and of potassium present in the residue may then be calculated from the following formulæ:—

$$\text{Weight of K} = \frac{[(A - B)1{\cdot}54] - B}{0{\cdot}63}$$

$$\text{Weight of Na} = \frac{B - [(A - B)0{\cdot}91]}{0{\cdot}63}$$

Where A = the weight of the mixed chlorides, and
B = the total weight of chlorine found in the chlorides.

The weight of each alkali-metal present is usually calculated as oxide, and not as chloride or as metal.

360. Limestone may also contain Phosphate, Sulphate, Chloride, and Carbonaceous Matter.—The phosphate may be estimated in the manner described under spathic iron-ore (372).

The sulphate may be estimated by dissolving 5 grams of the limestone in dilute hydrochloric acid, filtering off the residue, and precipitating the SO_4 as $BaSO_4$ (96).

The chloride may be estimated by dissolving 5 grams of the limestone in nitric acid, filtering off the residue, and precipitating and weighing the Cl as AgCl (113).

The amount of carbonaceous matter may be found by subtracting from the total loss of weight caused by ignition to redness, the weights of moisture (350), and of CO_2 (351).

For the Results obtained by the analysis of a limestone see Appendix.

Analysis of Spathic Iron-ore.

361. Spathic iron-ore consists essentially of impure ferrous carbonate. Its constituents are usually the same as those of limestone: but the proportion of ferrous carbonate is high, whereas the calcium and magnesium carbonates are present in small quantity only. Usually an appreciable quantity of manganese is present, and combined phosphorus and sulphur are frequently found. The amounts of phosphorus and of sulphur present must be carefully estimated; since the value of the ore, and the process of smelting it, are influenced by the proportions of phosphorus and sulphur which are present.

Preparation of the Ore.—Finely powder about 15 grams of the ore (34, 35), and keep the powder in a clean, dry stoppered bottle.

362. Estimation of Water.—Weigh out accurately about 2 grams of the powdered ore, and estimate the moisture in it by drying at 200° C. in the air-oven (350).

363. Estimation of Carbon Dioxide.—The amount of carbon dioxide is then estimated in the dry ore (362) by direct weighing (351).

364. Estimation of Silicious Matter.—The hydrochloric acid solution, together with the undissolved residue (**363**), is evaporated with a little strong nitric acid. The residue, consisting mainly of silica, is filtered off, washed, ignited, and weighed (**352**).

365. Estimation of Iron and Aluminium.—The filtrate from the silica (**364**) usually contains an appreciable amount of manganese. If such is the case, the iron and aluminium should be precipitated as basic acetates in the following manner. If manganese is absent refer to **353** for the method of precipitating the iron and the aluminium.

Dilute the acid filtrate (**364**) considerably with water; then add ammonium carbonate solution gradually, and with constant stirring, until the precipitate which forms at first is redissolved with difficulty. The colour of the solution will now have become deep brown. Continue the gradual addition of ammonium carbonate solution until a very slight precipitate forms, which just disappears when the liquid is stirred. This is known to be the case when the liquid remains slightly opalescent.

Now add a little acetic acid and a moderate quantity of ammonium acetate solution, and boil for a short time. Filter the liquid while it is hot (**71**, fig. 54), and wash the precipitate twice with boiling water. Remove any manganese, which has been precipitated with the iron and aluminium, by redissolving the precipitate in hydrochloric acid, adding ammonium carbonate as before, and reprecipitating the iron and aluminium with acetic acid and ammonium acetate solution as has been just described.

The precipitate will contain the iron and aluminium as basic acetates; the manganese will remain in solution. Filter, and wash the precipitate without intermission with hot water. Add the first portion of the washings to the two filtrates, and treat the liquid as is described later on. This liquid should be perfectly colourless.

366. Separation of the Iron from the Aluminium.—

The above precipitate (365) may be treated by either of the following methods in order to separate the iron from the aluminium.

(a). The precipitate is dissolved in dilute hydrochloric acid, and the iron and aluminium are estimated in the solution as is described in paragraph 354.

(b). The precipitate is dissolved in hydrochloric acid, and the solution is made up to 250 c.c. with water. Of this liquid 100 c.c. are measured out and are mixed with excess of ammonium hydrate solution. The precipitate, thus produced, is filtered off and is weighed as is described in paragraph 353. This will give the total weight of Fe_2O_3 and Al_2O_3 in 100 c.c. of the liquid. Keep this precipitate carefully.

The total amount of iron present is then estimated in another part of the solution. This is effected by reducing two separate portions of 25 c.c. each of the solution as is described in paragraph 261, or 262, and then titrating with the dichromate.

The weight of Fe_2O_3, corresponding to the Fe thus found, is calculated. The difference between the weight of the iron oxide thus found, and the weight of the iron oxide + alumina already determined, gives the weight of the alumina.

367. **Estimation of Iron present in the Ore in the Ferrous State.**—The larger part of the iron in the ore is probably present in the ferrous state. This is estimated by dissolving 3 grams of the ore in hydrochloric acid in the apparatus shown in fig. 68 (p. 185). The process of solution is carried out precisely as is described in par. 255, the ore taking the place of the steel there mentioned. By this procedure the ferrous compound present in the ore is dissolved without being changed into ferric salt. The ferrous salt in an aliquot part of this solution is then titrated by means of potassium dichromate solution (256).

368. Estimation of Manganese.—The filtrate from **365** contains the manganese, calcium, and magnesium. Add bromine-water to this solution until it acquires a permanent yellow colour; now add excess of ammonium hydrate solution, and warm. The manganese will be precipitated as hydrated peroxide. Filter this off, and add to the filtrate more bromine-water and AmHO to make sure that all the manganese is precipitated. Then wash the precipitate, dry and strongly ignite it, and weigh it as Mn_3O_4 (**129**).

369. Estimation of Calcium.—To the filtrate from **368** add a little ammonium oxalate solution. Allow the liquid to stand. Filter off, wash the precipitate, dry and strongly ignite it, and weigh as calcium oxide (**111**).

370. Estimation of Magnesium.—Evaporate the filtrate from the calcium oxalate precipitate (**369**) to dryness, ignite the residue, and estimate the Mg as $Mg_2P_2O_7$ (**130**).

371. Estimation of the Alkali-Metals.—The alkali-metals may be estimated, if necessary, as is described in paragraph **358**.

372. Estimation of Phosphate.—The estimation of phosphate in an iron-ore is of much importance. Two methods are described below, of which the second (**b**) is the more rapid and accurate.

(**a**). Any phosphate, which was present in the original ore, is precipitated with the basic acetates of iron and aluminium (**365**).

The precipitate of $Fe_2O_3 + Al_2O_3$ obtained in **366,b**, therefore, contains all the phosphate. Dissolve this precipitate by *prolonged* digestion with strong hydrochloric acid. Evaporate the solution to dryness on the water-bath, and dissolve the residue in nitric acid.

Add a large *excess* of ammonium molybdate solution (**449**), and allow the liquid to stand in a warm place for a few hours. Pour off the clear liquid, and treat it with

fresh molybdate solution to prove that all the phosphate has been precipitated. Filter off the yellow precipitate, and dissolve it in ammonium hydrate solution. Filter if necessary, add excess of magnesia mixture (132), and estimate the phosphate as $Mg_2P_2O_7$ (131).

(b). The phosphate may be estimated more rapidly as follows. Dissolve from 3 to 5 grams of the ore in nitric acid; boil off most of the acid: dilute, filter, and precipitate the (PO_4) from the filtrate by the addition of a *large excess* of ammonium molybdate solution (449). Treat this precipitate as is described above (a), and estimate the phosphate as $Mg_2P_2O_7$ (131).

373. **Sulphate and Chloride**, if they are present, may be estimated as is directed in par. 359.

For the Results obtained by the analysis of a spathic iron-ore, refer to the Appendix.

Analysis of Manganese-spar.

374. Manganese-spar consists mainly of manganese carbonate; but it usually contains small quantities of certain of the substances which are present in limestone (349).

Water, Carbon dioxide, Iron, and Aluminium are estimated as is described under spathic iron-ore (362, 363, 365, 366).

375. **Estimation of Manganese.**—The filtrate, from which the basic acetates of iron and aluminium have been precipitated (368), requires, however, the following special preliminary treatment.

The manganese is first precipitated from this filtrate as sulphide, MnS, by means of *colourless* ammonium sulphide solution. The sulphide solution is made as it is required, by passing hydrogen sulphide gas through ammonium hydrate solution.

For this purpose the filtrate from the basic acetates is neutralised with ammonium hydrate. A fair amount of ammonium chloride is then added, and a slight excess of the *colourless* ammonium sulphide. The liquid is then boiled for ten minutes. More ammonium sulphide is added, and the liquid is filtered through a double filter.

The precipitate is finally washed with water containing a little ammonium sulphide.

The precipitate of MnS may then be treated by either of the following methods.

(a). Dissolve the precipitate in hydrochloric acid, boil off any dissolved hydrogen sulphide gas, reprecipitate the manganese as carbonate, and weigh it as Mn_3O_4 (129).

(b). A quicker method consists in drying the precipitate of MnS in the steam-oven, and igniting it with the filter (73). It is then mixed with a little sulphur, heated in a current of hydrogen gas (67) until the precipitate becomes black, and weighed as MnS.

Calcium, Magnesium, Alkali-metals, Phosphate, Sulphate, and Chloride are estimated in the filtrate from the MnS (375), as is described in paragraphs 356, 357, 358, 359, 360.

Analysis of Salt-cake.

376. Salt-cake, or commercial sodium sulphate, usually contains small quantities of insoluble matter, iron, aluminium, calcium, magnesium, and chloride. For technical purposes the minor constituents are frequently determined directly, and the sodium sulphate is then estimated by difference.

377. **Estimation of Moisture.**—Salt-cake rarely contains any appreciable amount of moisture, since it is subjected to a red-heat during its preparation; and, moreover, crystallised sodium sulphate loses all its water of crystallisation on exposure to the air.

Weigh out 10 grams of the salt-cake, and heat it in the steam-oven for two hours. The loss of weight represents the adherent moisture.

378. **Estimation of Insoluble Matter.**—Treat the dried salt-cake (377) with hot water. Filter, and wash the residue with hot water until it is free from soluble sulphate. Dry the residue in the steam-oven, and ignite it together with the filter (73) at as low a temperature as possible.

Make up the filtrate and washings to 500 c.c. with water, shake well, and use aliquot portions of this solution for the estimations described below.

379. Estimation of dissolved Iron and Aluminium.—Measure out 200 c.c. of the solution (**378**) into a beaker, and heat it to boiling. Add a little ammonium chloride solution, and then sufficient ammonium hydrate to make the liquid smell faintly of ammonia after it has been well stirred. Filter, wash the precipitate and heat it to redness (**73**), and weigh as $Al_2O_3 + Fe_2O_3$. This precipitate is usually so small in amount, that the separate estimation of Al and of Fe is not necessary.

380. Estimation of Calcium.—To the hot filtrate (**379**) add a little ammonium oxalate solution, and allow the liquid to stand. Filter, wash the precipitate, ignite it, and weigh as calcium oxide (**111**).

381. Estimation of Magnesium.—Evaporate the filtrate (**380**) to dryness in a platinum or porcelain dish, and drive off the ammonium salts from the residue by ignition. Dissolve the residue in dilute hydrochloric acid, dilute with water, and filter if necessary.

To the clear solution add ammonium hydrate in moderate excess, and then a little sodium phosphate solution: and allow the liquid to stand for some hours. Filter, wash the precipitate with dilute ammonium hydrate solution, then ignite it, and weigh as $Mg_2P_2O_7$ (**130**).

382. Estimation of Sodium.—Measure 50 c.c. of the original solution (**378**) into a small beaker. Stir it with milk of lime, which must be added until the liquid is distinctly alkaline (**358**). Boil, filter off the precipitate and wash it twice. Precipitate the calcium from the filtrate and washings by adding ammonium hydrate in slight excess, then ammonium carbonate, and finally a small quantity of ammonium oxalate. Filter, and wash the precipitate.

Transfer the filtrate and washings to a platinum or porcelain dish, and evaporate the liquid after adding some sulphuric acid. As soon as nearly all the liquid is driven off, transfer it to a platinum crucible, and continue the evaporation to dryness. Ignite the residue, and weigh it as sodium sulphate (135).

383. **Estimation of Sulphate.**—Add to 50 c.c. of the original salt-cake solution (378) a little hydrochloric acid, and then barium chloride solution in excess. Filter; wash, dry, and ignite the precipitate, and weigh as $BaSO_4$ (96).

384. **Estimation of Chloride.**—Add to 100 c.c. of the original solution (378) a little dilute nitric acid. Then add silver nitrate solution in excess. Filter; wash, dry, and ignite the precipitate, and weigh as AgCl (113).

For the results of an Analysis of Salt-cake refer to the Appendix.

Analysis of Silicates, which can be Decomposed by Hydrochloric Acid.

385. Many natural silicates are completely decomposed when they are finely powdered, and are heated for some time with strong hydrochloric acid.

Many artificial silicates, such as the slags obtained in smelting iron, are also completely decomposed in this manner.

Natural silicates of this class usually consist of silicates of calcium and aluminium, and may also contain silicates of iron, manganese, magnesium, and the alkali-metals. Slags frequently contain in addition sulphides and phosphates.

If a part only of the silicate can be decomposed by hydrochloric acid, the silicate must be treated as an insoluble silicate and be fused with alkaline carbonates (390, 391).

386. **Estimation of the Silica.**—Weigh out accurately

from 1 to 1·5 grams of the finely-powdered silicate. Heat it with a little strong hydrochloric acid in a covered evaporating dish. As soon as the decomposition is complete, evaporate the liquid to dryness on the water-bath, with constant stirring (171), and heat the dish on the water-bath until no moisture condenses on a cold clock-glass, when it is placed as a cover over the dish.

Then treat the residue with hydrochloric acid, and filter off, wash, and weigh the silica as is described in paragraph 172, putting by the filtrate and washings for subsequent use.

A portion of the silica should be tested with hydrofluoric acid, to ascertain if it volatilises completely; if it does not, the remainder must be treated as an insoluble silicate (390, 391).

387. **Estimation of Iron, Aluminium, and Manganese.**—The method of procedure depends upon whether manganese is present or absent.

(a). *If Manganese is Absent*, add to the filtrate from the silica (386), first some ammonium chloride solution, and then ammonium hydrate in slight excess. Filter off, and wash the precipitate twice with water. Dissolve the precipitate in hydrochloric acid, and reprecipitate this solution as is directed in par. 353. Determine the weight of the precipitate (353), and proceed to separate iron from aluminium, if necessary, as is directed in par. 354.

(b). *If Manganese is Present*, precipitate the iron and aluminium together as basic acetates (365), and determine the manganese in the filtrate (368).

388. **Calcium, Magnesium, Alkali-metals, and Sulphate** are estimated as is directed in pars. 356, 357, 358, 359, 360; **Phosphate** by par. 372, and the total **Sulphur** by 408. The separation of silica must precede each of these estimations.

Analysis of Insoluble Silicates.

389. Most of the common silicates, such as felspar, mica, and garnet, contain the following metallic constituents:—aluminium, iron, calcium, magnesium, and the alkali-metals.

Directions for the analysis of the rarer silicates, such as beryl which contains beryllium, and petalite which contains lithium, will be found in larger treatises.

Practice in the analysis of an insoluble silicate may be obtained by analysing orthoclase or potash-felspar.

390. Preparation of the Silicate.—Powder very finely about 5 grams of potash-felspar in the following way. Fold a small quantity of the mineral in a piece of brown paper, and strike it sharply with a hammer on an iron anvil. This will break the felspar into fragments. Next coarsely powder these fragments by means of the percussion-mortar (35), and finally triturate these particles in the agate mortar until they are converted into an impalpable powder.

The success of the analysis largely depends upon the careful reduction of the substance to the finest powder. The powder can only be considered as suitable when it passes entirely through the finest of the brass sieves which are mentioned in paragraph 35.

391. Fusion with Alkaline Carbonates.—"A fusion" is next made as follows.

Weigh out accurately about 1·5 grams of the finely-powdered felspar into a platinum crucible. Add about six times its weight of finely-powdered fusion-mixture, consisting of sodium and potassium carbonates mixed in molecular proportions; and intimately mix these powders by means of a smooth rounded glass rod.

Unless the crucible is a capacious one, it will be found convenient to introduce the mixture little by little during the process of fusion, since the substance usually froths considerably. The mixture should never more than half fill the crucible.

Now place the lid on the crucible, and heat it gently over

the Bunsen-flame. Gradually increase the temperature, taking care that no loss is caused by frothing due to the evolution of carbon dioxide gas. As soon as the mass is fused, the crucible is transferred to the blowpipe-flame, and the whole is kept at a bright red-heat for at least fifteen minutes, or until effervescence ceases and the fused mass becomes tranquil.

392. Solution of the Metals.—Allow the crucible to cool just below redness, and place it on a cold surface, such as an iron plate, to induce rapid cooling. When it is cold, place the crucible and its contents in a deep evaporating dish or in a shallow beaker, and boil the mass with about 10 times its weight of water for half an hour: or let it stand in the water over night. Then cover the vessel with a clock-glass and gradually add tolerably strong hydrochloric acid. Gently agitate the contents of the beaker after each addition of the acid, and keep the beaker covered during the operation.

When the effervescence has ceased, and the crucible is free from all adherent solid, remove the crucible and its lid by means of a glass rod; and carefully rinse off any adhering liquid into the main portion of the liquid with a wash-bottle.

This treatment of the fused mass with acid will cause most of the silica to separate as a gelatinous mass. If any gritty particles are felt, on stirring the bottom of the vessel with a glass rod, the decomposition of the silicate has been incomplete. This is usually due to the original substance not having been sufficiently finely powdered. In this case it is usually best to start afresh, taking care that no coarse particles are present in the portion of the powdered mineral which is used for the fusion.

393. Estimation of Silica.—The liquid, containing the gelatinous silica, is then transferred to an evaporating dish, preferably of platinum, and is evaporated to dryness upon the water-bath. As soon as the contents of the dish become thick and pasty, they should be continually stirred with a rounded glass rod, in order to prevent the formation of lumps (**172**).

When all the liquid has been driven off, the contents of the dish should be in the state of a fine powder. Now place the dish in an air-bath (50,d), and heat it to 150°C., until no moisture is deposited on a cold clock-glass, when it is placed upon the dish for a few seconds.

The dish is then allowed to cool, and its contents are moistened with strong hydrochloric acid. After standing for some time it is heated on the water-bath for about half an hour, a small quantity of hydrochloric acid being occasionally added.

Hot water is now added, and the acid liquid is decanted off through a filter. This operation is repeated three times. The silica is finally transferred to the filter, and is washed free from dissolved chloride.

The precipitate is ignited apart from the filter (74); the precipitate being transferred to a platinum crucible cautiously, since it consists of very light powder, which is easily blown away. After placing the lid upon the crucible, it should be very gently heated at first, and the temperature is only gradually raised, else the escaping steam will carry some of the fine light powder away with it. The crucible is finally heated to full redness over the Bunsen-flame.

The purity of the silica should be tested as is described in paragraph 172.

394. **Estimation of Iron and Aluminium.**—The filtrate from 393 is mixed with ammonium chloride solution, and then with ammonium hydrate in slight excess; and the iron and aluminium hydroxides, of which the precipitate consists, are separated and estimated as is described in paragraph 354.

395. **Estimation of Calcium.**—If the volume of the filtrate from 394 is very large, evaporate it down to a convenient bulk. Then add a little ammonium hydrate, if the liquid is not already alkaline, and then a slight excess of ammonium oxalate. Allow the liquid to stand; filter off, ignite, and weigh the precipitate as oxide (III).

396. Estimation of Magnesium.—Evaporate the filtrate and washings from the calcium oxalate precipitate (395) to dryness, ignite the residue, and estimate the magnesium as is described in paragraph 357.

397. Estimation of the Alkali-Metals.—Since sodium and potassium carbonates have been used for the fusion, the alkali-metals cannot be estimated in the filtrate from the magnesium. A separate portion of the felspar is accordingly used for the determination.

Lawrence Smith's Method for the estimation of the alkali-metals may be employed. Proceed as follows.

Weigh accurately about 1·5 grams of the finely-powdered felspar into a platinum crucible. Intimately mix this with 1·5 grams of pure recrystallised ammonium chloride (80) and 9 grams of pure calcium carbonate (82).

Then heat the crucible to bright redness for an hour over a good Bunsen-flame or blowpipe-flame, or preferably as follows. Place the platinum crucible in a clay crucible containing a little calcined magnesia or lime at the bottom and round the sides, and heat the clay crucible in a gas-furnace, which is capable of maintaining it at a bright red-heat. When the crucible has been heated for an hour, allow it to cool.

Then place the platinum crucible and its contents in hot water in a covered platinum or porcelain dish, and boil for a time. This procedure will dissolve out the alkaline chlorides together with some calcium hydrate. Filter, and mix the filtrate with ammonium hydrate and ammonium carbonate solutions in excess, and then with a few drops of ammonium oxalate. Allow the liquid to stand, filter into a platinum or porcelain dish, evaporate the filtrate to dryness, and heat the residue short of redness, but sufficiently strongly to drive off the ammoniacal compounds.

Dissolve the residue in water; add a few drops of ammonium hydrate and of ammonium oxalate solution to precipitate any trace of calcium still in solution. Filter, and

evaporate the filtrate to dryness, with a few drops of HCl, in a weighed dish. Ignite the residue gently, and weigh it. Repeat the ignition until the weight is constant. The weight of the residue thus obtained gives the combined weight of the potassium and sodium chlorides.

The residue is then dissolved in water; and either the potassium chloride is estimated and the weight of the sodium chloride is found by difference (358, 1); or the total chlorine is determined either gravimetrically (113) or volumetrically (304), and the weights of the chlorides are calculated (358, 2).

The weights of the oxides corresponding to those of the chlorides found are then calculated.

For the Results of an Analysis, see Appendix.

Analysis of Glass.

398. Glass consists essentially of the same constituents as most of the natural insoluble silicates (389). Common glass is mainly composed of silicates of sodium and calcium; but it may also contain aluminium, iron, manganese, and potassium. In flint glass the calcium is replaced by lead.

The analysis of glass is carried out in the same way as the analysis of felspar (390–397). If, however, lead or manganese is present, the following special procedure is necessary.

Separate the silica as is described in paragraph 393. Pass hydrogen sulphide through the filtrate from the silica to precipitate the lead. Filter off, wash and dry the lead sulphide, and convert it into lead sulphate by heating it with strong nitric acid, and adding a little dilute sulphuric acid. Dilute, filter, and ignite the $PbSO_4$ (126).

Remove the excess of hydrogen sulphide from the filtrate by boiling it; then add a few drops of strong HNO_3 and boil; precipitate the iron and aluminium as basic acetates (365); and separate them, if necessary, as is described in paragraphs 354, 366.

Precipitate the manganese as the hydrated peroxide, by add-

ing bromine-water in excess, and then ammonium hydrate in excess, and boiling. Filter off the precipitate, ignite it, and weigh as Mn_3O_4 (375). The calcium and magnesium are estimated in the filtrate, as is directed in paragraphs 369, 370.

A separate fusion will be required for the determination of the alkali-metals, as in the case of insoluble silicates (397).

For Results of an Analysis of Glass, refer to the Appendix.

Analysis of Zinc-blende.

399. Blende, or "Black Jack," consists essentially of zinc sulphide; but this is commonly associated with galena or lead sulphide, and occasionally with calamine or zinc carbonate. The ore may also contain iron, aluminium, manganese, copper, and cadmium.

400. **Estimation of Moisture.**—The moisture present in "blende" is usually adherent only, and is not combined.

Weigh out accurately about 1·5 grams of the finely-powdered ore into the watch-glasses and clip. Heat this ore in the steam-oven until the weight becomes constant. The loss gives the amount of moisture.

401. **Solution of the Ore.**—Transfer the dried ore (400) to an 18-oz. beaker, covered with a clock-glass. Add a little strong hydrochloric acid, and heat gently for some time. If any carbonate is present, the ore will effervesce as soon as the acid is added.

When hydrogen sulphide ceases to be evolved, add more strong hydrochloric acid and about an equal volume of nitric acid. As soon as the ore is completely dissolved, transfer the liquid to a porcelain dish, and evaporate to dryness on the water-bath.

402. **Estimation of Silicious Matter and Lead.**—Heat the residue for some time in the air-bath at 150° C. to render the silica insoluble. Then moisten the residue with strong

hydrochloric acid, and dilute with a little water. Next add a few c.c. of strong sulphuric acid, and heat gently on the sand-bath until the hydrochloric and nitric acids are removed, and white fumes of H_2SO_4 are evolved. Again dilute with water, and filter. Wash the residue with water containing a few drops of sulphuric acid, and finally with methylated spirit, until all the acid is removed. Add the first washings to the filtrate, but reject the alcoholic washings.

The residue on the filter consists of gangue or earthy matter, silica, and lead sulphate. Dry the residue in the steam-oven, ignite the precipitate and filter apart (74–78), convert any lead, which has been reduced by the incineration of the filter, into sulphate (126), and weigh the residue.

Dissolve out the lead sulphate by boiling the residue with ammonium acetate solution made alkaline with ammonium hydrate. Repeat this treatment with fresh portions of the solvent until no lead can be detected in a drop of the acetate solution, when it is tested with ammonium sulphide. Again dry the residue, then ignite (73) and weigh it as silicious matter.

The loss of weight which the residue has suffered by being treated with the ammonium acetate solution represents the amount of lead sulphate which it contained.

403. Estimation of Copper.—To the filtrate from the above residue (402) add a little dilute hydrochloric acid, and saturate the liquid with hydrogen sulphide. Then filter at once, keeping the funnel covered with a glass plate, and washing rapidly with water containing a little hydrogen sulphide. These precautions are necessary in order to prevent the oxidation of the CuS into soluble $CuSO_4$ by exposure to the air. The filtrate and washings should be tested with hydrogen sulphide, to ascertain that they contain no copper in solution.

The copper is then estimated as cuprous sulphide, Cu_2S. For this purpose, the precipitate is dried in the steam-oven. The filter is burnt in a Rose's crucible (67), the precipitate

is added together with some powdered redistilled sulphur, and the mixture is heated in a current of hydrogen as long as sulphur vapour escapes. The Cu_2S is allowed to cool in the stream of hydrogen, and is weighed (425).

404. Estimation of Cadmium.—If any cadmium is present in the ore, the precipitate obtained by hydrogen sulphide will contain both CuS and CdS. This precipitate is boiled with dilute sulphuric acid, in order to dissolve out the CdS. The copper, which remains as sulphide, is estimated as is described above. The acid filtrate, containing the cadmium, is neutralised with ammonium hydrate; and the cadmium is precipitated as sulphide by passing hydrogen sulphide gas. The CdS is then estimated as is described in paragraph 155.

405. Estimation of Iron.—Boil off the hydrogen sulphide from the above filtrate (404) and add barium chloride solution in sufficient quantity to precipitate the whole of the sulphate present. Filter, and add ammonium carbonate to the filtrate, drop by drop, until a *very faint* permanent turbidity remains after the liquid has been well stirred. Now add ammonium acetate solution containing a little free acetic acid, and boil.

Filter the boiling liquid, using the funnel-jacket (fig. 55, p. 71). Wash the precipitate twice, and redissolve it in hydrochloric acid. Add ammonium carbonate and reprecipitate the iron with ammonium acetate, as is described above. Filter, wash, dry, and ignite the precipitate (73), and weigh the iron as Fe_2O_3.

The above double precipitation is necessary in order to remove small quantities of zinc and manganese which are precipitated with the iron.

406. Estimation of Manganese.—Treat the filtrates and washings from 405, which contain both the manganese and the zinc, with a little bromine-water; then add excess of ammonium hydrate, and boil. Filter off the precipitate; wash, dry, and ignite it; and weigh as Mn_3O_4.

407. Estimation of Zinc.—The filtrate and washings from **406**, which contain the zinc, may be treated in one of three ways.

(a). The liquid may be made up to a known volume, and then be titrated with sodium sulphide solution (**307**).

(b). Or the zinc may be precipitated as sulphide by adding a slight excess of colourless ammonium sulphide; it is then weighed as ZnS (**438**).

(c). Or the ZnS, instead of being weighed as such, may be dissolved in hydrochloric acid; and, after the excess of H_2S has been boiled off, the zinc may be precipitated as carbonate, and weighed as oxide (**128**).

408. Estimation of Sulphur. — Weigh out accurately about 1 gram of the *finely-powdered* ore into a platinum or nickel crucible. Mix this intimately with six times its weight of *finely-powdered* sodium peroxide (**104**). Heat the crucible over a small Bunsen-flame, gradually raising the temperature until the mass fuses. Maintain the substance in a fused condition for three minutes.

Extract the cold mass with water, remove lead, if present, by acidifying the solution with nitric acid, and boiling with excess of sodium carbonate solution. Filter, wash the residue, acidify the filtrate and washings with dilute hydrochloric acid, and estimate the sulphate in solution as $BaSO_4$.

409. Estimation of Carbon Dioxide.—If carbonate is present, it may be determined by acting upon 4 grams of the finely-powdered ore with dilute sulphuric acid, in the apparatus which is described in paragraph **140**.

For the Results of an Analysis, see Appendix.

Analysis of Galena.

410. Galena consists essentially of lead sulphide; but it may also contain silicious matter, silver, copper, antimony, and zinc.

411. Estimation of Moisture.—The moisture present in galena is hygroscopic, and is usually small in amount. Weigh out accurately about 1·5 grams of the *finely-powdered* ore, and heat it in the steam-oven until its weight becomes constant.

412. Estimation of Silicious Matter and Lead.—Dissolve the dry ore (**411**) in fuming red nitric acid, of 1·5 specific gravity. This operation is best performed in a 10-oz. flask, in the neck of which a small funnel is placed (fig. 28, p. 40). Heat the contents of the flask until all the sulphur is oxidised, and the lead is converted into lead sulphate.

Add a small quantity of sulphuric acid and evaporate the liquid together with the undissolved matter in a dish. Then heat the residue on the sand-bath until dense white fumes appear, so as to render the silica insoluble. Dilute with water, filter, wash the residue with water containing sulphuric acid, using as little washing-water as possible. Finally wash with methylated spirit until all the acid is removed, and reject the alcoholic washings.

Ignite the residue apart from the filter (**74–78**) in a porcelain crucible, and dissolve away the lead sulphate from the gangue by means of alkaline ammonium acetate solution, as is described in paragraph **402**.

413. Estimation of Silver.—To the filtrate from the silica and lead (**412**) add a few drops of hydrochloric acid, and allow the liquid to stand in a warm place for several hours. Filter, wash the silver chloride precipitate, and determine its weight (**123**).

A percentage of silver as low as 0·001 may be profitably extracted from galena. Hence great care must be taken to determine accurately even minute amounts of silver in this ore. Another method for estimating the silver is described in paragraph **303**.

414. Estimation of Copper.—Into the filtrate from the

silver chloride pass hydrogen sulphide gas to saturation. Allow the liquid to stand, and filter off the precipitated sulphides of copper and antimony. Wash the precipitate with water containing hydrogen sulphide as expeditiously as possible, taking care to cover the funnel with a glass plate, so as not to expose the precipitate unnecessarily to the atmosphere.

Digest the precipitate on the water-bath for half an hour with sodium sulphide solution, prepared as is directed in par. **307**, add water, and filter. Ammonium sulphide cannot be used, since CuS is slightly soluble in this reagent. The precipitate left on the filter will consist of copper sulphide; determine the copper as Cu_2S (**425**).

415. Estimation of Antimony.—The filtrate will contain the antimony. Acidify it with hydrochloric acid, then saturate it with H_2S: filter off the antimony sulphide, convert it into Sb_2O_4 (**160**), and weigh it as such.

416. Estimation of Iron and Aluminium.—Boil off the hydrogen sulphide from the filtrate, add a few drops of nitric acid to convert the iron into the ferric state, then add ammonium chloride solution and a slight excess of ammonium hydrate. Filter, wash the precipitate twice, redissolve it in hydrochloric acid, and precipitate this solution again with ammonium hydrate. Filter off the precipitate, dry and ignite it, and weigh as Fe_2O_3 (**92**).

417. Estimation of Zinc.—To the hot filtrate add a slight excess of colourless ammonium sulphide, boil, and estimate the Zn as ZnS (**438**).

418. Estimation of Sulphur.—Weigh out accurately 1 gram of the *finely-powdered* galena. Fuse it with sodium peroxide and estimate the sulphur as is described in par. **408**.

For the Results of an Analysis, see Appendix.

Analysis of Copper-pyrites.

419. Copper-pyrites is the most common ore of copper. It consists of a double sulphide of copper and iron, having the formula $CuFeS_2$. The ore, however, usually contains silicious matter and small quantities of lead, bismuth, arsenic, antimony, manganese, and zinc, and occasionally nickel and cobalt.

A qualitative analysis of the ore should always precede the quantitative estimations.

Estimation of Moisture.—The finely-powdered pyrites is heated in the steam-oven until its weight becomes constant.

420. Estimation of Insoluble Matter.—Weigh out accurately about 1 gram of the ore into a porcelain evaporating dish. Pour upon it a mixture of 3 parts of nitric acid and 1 part of hydrochloric acid; cover the dish with an inverted funnel to prevent loss by spirting, and heat it on the water-bath. As soon as all the sulphur, which separates out at first, is dissolved, evaporate to dryness twice with HCl in order to remove the HNO_3 and to render the silica insoluble.

Moisten the residue with strong hydrochloric acid, add water, and filter off and wash the residue. The residue will consist of silica and gangue, and will probably contain some lead sulphate. Dissolve out the latter with alkaline ammonium acetate solution (**402**), and add this solution to the acid filtrate. The residue is then ignited (**73**) and weighed.

421. Estimation of Sulphur.—One of the following methods may be used.

(a). Add to the filtrate from **420** a little tartaric acid to prevent the precipitation of iron and aluminium, heat it to boiling, and precipitate the sulphate with barium chloride; filter, and wash and weigh the $BaSO_4$ (**96**).

(b). A more rapid method of estimating the sulphur consists in fusing a mixture of 1 gram of the finely-powdered ore with sodium peroxide (**408**).

422. Estimation of Copper, Lead, Arsenic, and Antimony in the hydrogen sulphide precipitate.

Lead.—Dissolve 2 grams of the powdered ore in red fuming nitric acid, of 1·5 specific gravity; add a few c.c. of strong sulphuric acid, and evaporate until dense white fumes appear. Treat the residue with hydrochloric acid, add water, and allow it to stand. Filter, and wash the residue, and estimate the lead sulphate as is directed in paragraph **402**.

Pass hydrogen sulphide through the filtrate to saturation. Copper, lead, arsenic, and antimony sulphides will be precipitated. Filter; pass H_2S again through the boiling filtrate, and pour it again through the filter, if necessary. Wash the precipitate with water containing hydrogen sulphide, reserving the filtrate and washings for **423**.

Arsenic and Antimony.—Heat the precipitate with sodium sulphide solution (**307**) to dissolve the antimony and arsenic sulphides, dilute and filter.

Acidify the filtrate with HCl, pass H_2S, and filter. Dissolve the sulphides by heating them with HCl and a little $KClO_3$. Add tartaric acid and AmCl solutions, to keep the Sb in solution. Then add excess of AmHO. No precipitate will form, if sufficient $H_2\bar{T}$ and AmCl have been added. Add magnesia mixture (**132**), and determine the As as $Mg_2As_2O_7$ (**134**).

Precipitate the Sb from the filtrate by hydrogen sulphide as Sb_2S_3, and determine it as Sb_2O_4 (**160**).

Lead.—Dissolve the precipitate, containing the copper and lead sulphides, in nitric acid. Evaporate the solution nearly to dryness, dilute with water, add a few drops of dilute sulphuric acid, and allow the liquid to stand. Filter, and wash the lead sulphate with a little water acidified with

sulphuric acid. Finally wash out the acid from the filter with methylated spirit, rejecting the alcoholic washings. Then ignite and weigh the $PbSO_4$ (**126**), and add the weight to that already obtained.

Copper.—The copper in the filtrate may either be precipitated by sodium hydrate and estimated as CuO (**90**), or it may be precipitated as CuS by hydrogen sulphide and estimated as Cu_2S (**425**).

423. Estimation of Iron, Manganese, and Zinc.—The original hydrogen sulphide filtrate is oxidised with a little nitric acid, and the metals are precipitated and estimated as is described under zinc-blende (**405–407**).

For the Results of an Analysis, see Appendix.

Analysis of Brass.

424. Brass is an alloy consisting mainly of copper and zinc, but small quantities of lead and iron are usually present.

Preparation of the Sample.—The sample for analysis should be taken with a drill, since if a file is employed its teeth are apt to be broken off, and to increase the proportion of iron in the filings.

Solution of the Alloy.—Dissolve 2 grams of the metal in 10 c.c. of nitric acid (1·42 sp. gr.) in a lipped beaker covered with a clock-glass. When all action has ceased, remove and rinse the clock-glass, add 10 c.c. of concentrated sulphuric acid, and evaporate until sulphuric acid fumes are evolved. Then cool, dilute with cold water to 150 c.c., filter from $PbSO_4$, and dilute the filtrate to 500 c.c.

425. Estimation of Copper.—To 250 c.c. of this solution, which is equal to 1 gram of the alloy, add 40 c.c. of hydrochloric acid (1·1 sp. gr.), dilute with boiling water to about 500 c.c. in a large beaker, and pass H_2S through the boiling

liquid for half an hour. Filter, and wash the precipitate four times with warm H_2S water.

Redissolve the precipitate in nitric acid, to which a little bromine has been added, in a covered porcelain basin, and remove the excess of nitric acid and bromine by evaporation over a steam-bath. Dissolve the residue in 40 c.c. of hydrochloric acid (1·1 sp. gr.), transfer the solution to the beaker, dilute with hot water to about 500 c.c., and reprecipitate the copper with H_2S.

This double precipitation of the copper is necessary in order to separate a small quantity of ZnS which is precipitated with the CuS.

Filter, thoroughly wash the precipitate with H_2S water until the washings, after being freed from H_2S by boiling, give no milkiness with silver nitrate solution.

Estimation of Cu as Cu_2S.—Dry the precipitate, detach it from the filter, burn the filter in a Rose's crucible (67), then add the precipitate together with a little powdered redistilled sulphur, cover the crucible with the lid and tube, and pass a gentle stream of pure dry hydrogen.

Heat the crucible at first gently, until the flame of burning sulphur has nearly disappeared, then raise the temperature to full redness, and finally ignite strongly with the blowpipe for about five minutes. Let the precipitate cool in hydrogen until the crucible can be handled with comfort, allow it to cool in the desiccator, and weigh it. Then add a little more pure sulphur and repeat the ignition in hydrogen until the weight is constant.

From the weight of Cu_2S thus obtained, the percentage of Cu is calculated.

An Alternative Method of determining the copper is to precipitate it as cuprous sulphocyanide (338) from 50 c.c. of the original solution of the alloy (424). See also pars. 330, 331.

426. Estimation of Zinc.—Boil down the filtrates and washings from the CuS precipitate (425) in a large basin, finishing the evaporation over a steam-bath, until all the hydro-

chloric acid is expelled, and sulphuric acid is the only free acid remaining. Dilute with water to about 300 c.c., add a solution of pure sodium hydrate until the acid is nearly neutralised, then add pure solid sodium carbonate in excess and boil.

Filter off the precipitate of $ZnCO_3$ and $Fe_2(OH)_6$, wash with boiling water until the washings give no trace of cloudiness with barium chloride solution even after standing. Dry the precipitate, and ignite and weigh it as ZnO (**128**).

Deduct from this weight the weight of Fe_2O_3 which is found in **428**, and calculate the percentage of Zn.

427. Estimation of Lead.—Dissolve 5 grams of the alloy in 20 c.c. of nitric acid (1·42 sp. gr.), stir in gradually 15 c.c. of concentrated sulphuric acid, and evaporate the liquid with constant stirring until sulphuric acid fumes are copiously evolved. Cool the residue and dilute it with cold water to 225 c.c., stir until all is dissolved except $PbSO_4$. Filter, and wash with water containing one-fifteenth of strong sulphuric acid, until the copper is removed. Then wash out the acid from the filter with alcohol, rejecting the alcoholic washings.

Finally dry, ignite, and weigh the $PbSO_4$ (**126**), and from this calculate the percentage of Pb.

428. Estimation of Iron.—Add to the filtrate and the washings from **427** a large excess of ammonia and filter. Wash with water containing ammonia until the washings cease to be blue. Dissolve the precipitate on the filter with hydrochloric acid, and wash the filter with cold water. Dilute the solution and washings to about 200 c.c., add ammonia solution to the *cold* liquid until it is nearly neutralised, but no permanent precipitate is formed.

Then add some ammonium acetate and boil. Filter, using the same filter as before, and wash the precipitate. Again dissolve the precipitate in hydrochloric acid, and precipitate the ferric hydrate by adding ammonia solution. This re-precipitation is necessary to remove zinc from the ferric hydrate.

Finally filter; wash the precipitate, dry and ignite it, and weigh as Fe_2O_3 (92). From this weight calculate the percentage of Fe.

For the Results of an Analysis, see Appendix.

ANALYSIS OF ALLOYS CONTAINING TIN AND ANTIMONY.

429. Ordinary bronze is an alloy consisting chiefly of copper and tin, but other metals may be present as well. Type-metal consists mainly of lead, antimony, and tin; it may also contain traces of copper and of iron.

430. **Precipitation with Hydrogen Sulphide.**—Dissolve 1 gram of the alloy in aqua regia, add 10 grams of pure tartaric acid dissolved in a little hot water, and make the solution alkaline by the addition of pure sodium hydrate* solution. Pour this liquid into a basin containing 30 grams of pure sodium hydrate dissolved in about 500 c.c. of water. Heat the liquid until it boils gently, pass a rapid stream of H_2S until the liquid is saturated, keeping the basin covered with a perforated glass plate. Filter, wash the precipitate with hot dilute sodium sulphide solution (307), and wash it finally once with boiling water. Reserve the filtrate and washings for par. 432.

431. **Estimation of Lead, Copper, Zinc, and Iron.**—Dissolve the precipitated sulphides from 430 in nitric acid, evaporate until the liquid becomes syrupy, dilute with water, filter off any traces of SnO_2 which may have been originally precipitated as sulphide by H_2S, and reserve this precipitate to be added to the main quantity of SnS.

Assuming that the filtrate contains lead, copper, zinc, and traces of iron, these metals may be estimated by evaporating with sulphuric acid to separate lead (427), then precipitating the copper from the filtrate with H_2S (425), and finally

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* The pure sodium hydrate required for this purpose may be made by boiling "ammonia soda" with slaked lime and water.

throwing down the zinc and iron with sodium carbonate (426, 428).

432. Estimation of Antimony. — Make the alkaline filtrate from 430 distinctly acid with hydrochloric acid, which must be added cautiously and with continual shaking, and allow the liquid to stand at a gentle heat until the precipitate has completely separated. Filter, and wash the precipitate four times with cold H_2S water, letting the washing-water drain away completely each time. If the precipitate shows any tendency to pass through the filter, add a little NaCl to the washing-water.

Remove the precipitate from the filter, with a platinum spatula, into a porcelain basin, using hot hydrochloric acid to dissolve off the traces which adhere to the paper. Pour some more hydrochloric acid into the basin, cover it, and heat gently, adding occasionally a small crystal of potassium chlorate. Seven parts of the chlorate must be used for one part of tin or of antimony. Boil the liquid gently to expel chlorine, remove the cover, rinsing it into the dish, filter into a flat porcelain dish and evaporate to about 5 c.c.

Note.—The $KClO_3$ is added to form double chlorides with the Sn and Sb which are not decomposed by evaporation, so that no $SnCl_4$ or $SbCl_5$ is lost even by evaporation to dryness.

Add a clear hot solution containing 20 grams of pure oxalic acid, transfer the liquid to a tall beaker, dilute with boiling water to 300 c.c., and pass a rapid current of H_2S through the boiling solution until the Sb_2S_3 has completely separated. This usually requires about twenty minutes. Filter at once on a weighed ribbed filter, wash thoroughly with hot water, and dry.

Digest the dry filter and precipitate in some pure carbon disulphide contained in a very small beaker, to dissolve out free sulphur (156). Then place the filter in a funnel and wash with CS_2. Dry the filter and contents at a gentle heat to expel CS_2, and then at 130° C. till constant in weight. Refer to par. 160 for a method which avoids charring the filter.

From the weight of Sb_2S_3 thus obtained, calculate the percentage of Sb in the alloy.

433. Estimation of Tin.—Before the tin is precipitated from the filtrate from **432**, it is necessary to destroy the oxalic acid. For this purpose transfer the liquid to a large porcelain basin, add hydrochloric acid in excess, heat, cover the basin, and add solid $KMnO_4$ by degrees until a small precipitate of MnO_2 remains, which does not dissolve on boiling even when more hydrochloric acid is added. Redissolve the MnO_2 by adding a few drops of $FeSO_4$-solution, then pour the clear hot solution into a flask, and pass H_2S to precipitate the tin.

Allow the precipitate to settle, syphon off the clear liquid, collect the precipitate on a filter, and wash it with H_2S-water containing a little ammonium nitrate. After the precipitate of SnS mixed with S has been thoroughly washed, dry it, convert it by ignition in an open crucible into SnO_2 (**163**), and weigh this.

From the weight of SnO_2 thus obtained, the percentage of Sn in the alloy is calculated.

For Results of Analysis, see Appendix.

Analysis of German-silver.

434. German-silver is an alloy of copper, zinc, and nickel, and frequently contains traces of tin and of iron.

For the estimation of these constituents, weigh out accurately about 1 gram of filings, or better, drillings or borings of german-silver. Dissolve this in nitric acid, and evaporate nearly to dryness to remove most of the acid.

435. Estimation of Tin.—Treat the residue with water; and if any appreciable quantity of SnO_2 remains undissolved, filter off and weigh it (**164**).

436. Estimation of Copper.—Precipitate the copper from the filtrate (**435**) by passing hydrogen sulphide. Dissolve

the CuS in dilute HNO_3, and reprecipitate it with hydrogen sulphide, observing the precautions described in paragraph **425**, and weigh the copper as Cu_2S (**425**).

437. Estimation of Iron.—Boil off the hydrogen sulphide from the filtrate (**436**), and add a few drops of strong nitric acid to convert the iron into the ferric condition. Add ammonium chloride solution, and precipitate the iron by a slight excess of ammonium hydrate. Redissolve the precipitate in a little HCl, and again precipitate by ammonia. Filter off, wash and ignite the precipitate; and weigh as Fe_2O_3 (**92**).

438. Estimation of Zinc.—Acidify the filtrate (**437**) with HCl: add Na_2CO_3 solution until a faint permanent precipitate is formed; and redissolve this by adding a few drops of HCl. Pass hydrogen sulphide as long as any precipitate forms; then add a few drops of very dilute ammonium acetate solution, and pass H_2S gas again to saturation. The ZnS thus precipitated is heated to render it granular; it is then filtered off and washed with hot water, and is weighed either as such (**a**) or as oxide (**b**).

(**a**). Dry the precipitate of ZnS in the steam-oven, and transfer it to a porcelain crucible fitted with Rose's lid and tube (**67**); incinerate the filter, and add the ash. Sprinkle a little sulphur over the contents of the crucible, and ignite in a current of dried hydrogen gas. The temperature should be low at first, but should be gradually increased to an intense red-heat. Weigh the ZnS.

(**b**). Another method is to dissolve the freshly-precipitated ZnS in hydrochloric acid, boil off the H_2S, precipitate the Zn as carbonate, and weigh as ZnO (**128**).

439. Estimation of Nickel.—Acidify the filtrate with a little HCl, boil off the hydrogen sulphide, precipitate the nickel with sodium hydrate solution, and weigh as NiO (**91**).

For Results of Analysis, see Appendix.

Analysis of Iron-ores.

440. The ordinary ores of iron are either oxides or carbonates. The common oxide-ores are red and brown hæmatite, and the black or magnetic oxide. The carbonate usually occurs as spathic iron-ore (**361**) and clay iron-stone, which usually contain both oxide and carbonate.

Iron-ores may contain the following constituents: moisture, carbon dioxide, silica, iron, aluminium, manganese, calcium, magnesium, phosphate, and sulphate. Some ores also contain organic matter.

441. Estimation of Moisture.—Since carbon dioxide and organic matter are usually present, the water must be estimated by heating 2 grams of the ore to dull redness, and absorbing the water evolved in calcium chloride, as is directed in paragraph **154**.

442. Estimation of Carbon Dioxide.—Estimate the carbon dioxide by absorption as is described in paragraph **140**. Use 2 grams for the determination.

443. Estimation of Silicious Matter.—Weigh accurately about 10 grams of the finely-powdered ore. Heat it gently with strong hydrochloric acid, add a little nitric acid, and continue the heating until it is judged that all soluble matter has been dissolved. Then evaporate to dryness on the water-bath, and heat to 150° C. on the air-bath (**50, d**).

Treat the residue with strong hydrochloric acid, dilute, and decant off the clear liquid through a filter. Treat the residue again with a small quantity of hydrochloric acid and filter the solution. Continue this treatment as long as any iron can be found in the acid. Finally filter, wash and ignite the residue (**73**), and weigh it as silica and gangue.

The filtrate and washings are transferred to a half-litre flask, and are diluted to 500 c.c. This liquid serves as the "original solution" which is used for the other estimations.

444. **Estimation of Aluminium.**—Boil 50 c.c. of the original solution (443) with a little nitric acid to convert the iron into the ferric state, nearly neutralise the liquid with ammonium carbonate, and precipitate the iron by means of ammonium acetate solution (365).

Filter, and wash, ignite, and weigh the precipitate. The ignited precipitate will consist of Al_2O_3,Fe_2O_3, and a little ferric phosphate. The weight of Al_2O_3 is subsequently found by subtracting the weight of the Fe_2O_3 and P_2O_5 from the total weight of the ignited precipitate.

445. **Estimation of Iron.**—Reduce the iron in 50 c.c. of the original solution (443) from the ferric to the ferrous condition by one of the methods described in pars. 260–262. As soon as the iron has been completely reduced, make up the solution to 250 c.c. with air-free water, and titrate it with potassium dichromate (256). Iron present in the ferrous state may be estimated as is directed in par. 367.

446. **Estimation of Manganese.**—Treat 200 c.c. of the original solution as is directed in par. 444. To the filtrate from the basic acetates, which has been concentrated if necessary by evaporation, add bromine-water in slight excess, and then a few drops of ammonium hydrate, and warm. Filter, and wash the manganese precipitate; then ignite it and weigh as Mn_3O_4 (129).

447. **Estimation of Calcium and Magnesium.**—These metals are estimated in the filtrate from 446 in the way described in paragraphs 356, 357; but a *single* precipitation with ammonium oxalate will suffice.

448. **Estimation of Phosphate.**—If arsenic has been found in the qualitative analysis, it must be separated by means of hydrogen sulphide (451) before precipitating the phosphate.

To 50 c.c. of the original solution, or 250 c.c. if the phosphorus is below 0·2 per cent., add a moderate quantity of ammonium molybdate solution (449), and allow the liquid to stand in a warm place for some hours. Filter, after prov-

ing that the precipitation is complete (466). Then dissolve the yellow ammonium phospho-molybdate precipitate in ammonium hydrate; precipitate the phosphate with magnesia mixture (132), and weigh it as $Mg_2P_2O_7$ (131).

449. *Preparation of Ammonium Molybdate Solution.*—Pour 100 c.c. of water into a large flask, add 50 grams of molybdic acid, then 100 c.c. of ammonia (sp. gr., 0·88); stir the liquid until all is dissolved, then pour the solution quickly into 720 c.c. of cold nitric acid (sp. gr., 1·2), stirring during the addition. Keep the liquid in a warm place for some hours, and decant the clear liquid for use.

450. **Estimation of Sulphur.**—Evaporate 50 c.c. of the original solution nearly to dryness, so as to expel almost all the free acid; dilute, and precipitate with a little barium chloride solution. Allow the liquid to stand several hours; and filter off, ignite, and weigh the $BaSO_4$ (96).

451. **Estimation of Copper, Arsenic, and Antimony.**—During the evaporation of the acid solution (443) some of the arsenic will have volatilised. Therefore a fresh portion of the ore is dissolved in hydrochloric acid, and the sulphides of the above metals are precipitated, after dilution, by means of H_2S; they are then separated as is directed in paragraph 422.

For Results of Analyses, see Appendix (763).

Analysis of Iron and Steel.

452. The description of the analysis of cast-iron may be taken as typical of the method of analysing the various kinds of iron.

The common impurities of iron are present in cast-iron in greater quantity than in either wrought-iron or steel. It follows that a larger quantity of wrought-iron or of steel must be taken for analysis than is necessary in the analysis of cast-iron.

The estimations which are usually made for ascertaining the value of a sample of iron or steel are those of free and combined carbon, silicon, phosphorus, manganese, sulphur, and copper. In certain kinds of steel or iron other constituents may be estimated, such as titanium, chromium, aluminium, tungsten, and arsenic.

The following analyses will give some idea of the average percentage proportion of the constituents which are usually present in cast-iron, wrought-iron, and steel :—

	Bessemer Pig-iron.	Wrought-iron.	Bessemer Steel.
Iron, ...	93·301	99·13	99·445
Graphite, . . .	2·930	...	...
Combined carbon,	0·618	0·15	0·234
Silicon, ...	2·72	0·14	0·033
Sulphur, . . .	0·062	0·04	...
Phosphorus, . .	0·039	0·47	0·044
Manganese, . .	0·105	0·14	0·139
Copper, ...	0·010	...	0·105
Arsenic, . . .	0·075	...	...

It will be noticed that, as a rule, cast-iron contains carbon both in the combined state and in the free state as graphite.

453. Estimation of Total Carbon.—Of the many methods which have been devised for the estimation of the total carbon present in iron, the most trustworthy are those which depend upon the separation of the carbon as such, and its subsequent conversion into carbon dioxide: the carbon dioxide being then absorbed and weighed. Two methods are described below (454, 456), of which the second (456) is the more accurate.

454. Ullgren's Method for Estimating Total Carbon.—The carbon is separated by immersing the iron, in the form of crushed powder or borings, in copper sulphate solution. The iron passes into solution, and an equivalent amount of copper is deposited. The copper remains as a residue together with the carbon; a minute portion of the carbon, however, usually escapes in the form of hydrocarbon gases. The carbon is then converted by means of chromic acid into carbon dioxide: and this is absorbed by soda-lime and weighed.

The Process of Estimation.—Weigh out accurately about

2 grams of the cast-iron into a small beaker. If the proportion of carbon is low, the weight of iron used must be proportionately increased. Pour upon the cast-iron a solution of copper sulphate, made by dissolving 1 part of the crystallised salt in about 6 parts of water, and allow the beaker to stand in a warm place.

When the iron has completely dissolved, no hard particles will be felt by the end of a glass rod. Then pour off the clear liquid, and transfer the copper together with the carbon to an 8-oz. round flask, by means of a glass rod and a *small quantity* of water. Now add about 50 c.c. of strong sulphuric acid, and 10 grams of chromic anhydride crystals (455). Connect the flask with the tubes shown in fig. 57 (p. 117), of which (*f*) is weighed, and try if the apparatus is gas-tight.

Gradually raise the temperature of the flask, until the bubbles of gas which pass through the bulb-tube (*d*) can just be counted. As the evolution of gas slackens, increase the temperature until white fumes are observed in the flask.

When this is the case, aspirate a slow current of air through the apparatus. As soon as a volume of air equal to about six times the capacity of the flask has passed, the U-tube (*f*) is detached and weighed. From its increase of weight the amount of carbon dioxide is found, and from this the weight of carbon oxidised by the chromic acid may be calculated.

455. *Preparation of Chromic Anhydride.*—Make a saturated solution of potassium dichromate, and mix this with an equal volume of strong sulphuric acid in a large beaker. Allow the liquid to cool, and pour off the mother-liquor from the crystals which have formed. Drain the crystals in a covered funnel, the neck of which is plugged with glass-wool, and place them in a bottle. A further crop of crystals may be obtained by evaporating down the mother-liquor, and allowing it to cool.

456. Second Method for the Estimation of Total Carbon.—The powder or borings of the metal are digested with excess of cupric-ammonium-chloride solution. The iron is thus dissolved, while an equivalent weight of copper is precipitated. If the digestion, however, is continued suf-

ficiently long, the copper is redissolved, and a residue of carbon only remains. The carbon is then ignited in a current of oxygen, and the carbon dioxide thus produced is absorbed by soda-lime and weighed.

Preparation of the Cupric Ammonium Chloride Solution.—Dissolve 53 grams of pure ammonium chloride, and 85 grams of pure recrystallised copper chloride, in about 500 c.c. of water. Keep this solution in stoppered bottles.

The Process of Estimation.—Weigh out accurately from 1 to 3 grams of the iron, and digest it with from 50 to 250 c.c. of the cold cupric-ammonium-chloride solution. Stir with a glass rod until complete disintegration is effected. The residue will consist of carbon and metallic copper.

Continue the digestion at a temperature of 70° C., until all the copper is dissolved, adding more of the copper solution, if necessary. If a scum of basic ferric chloride forms upon the surface of the liquid, add a little hot dilute hydrochloric acid. As soon as the copper is completely dissolved, which is known by the residue not feeling gritty under a glass rod, collect the carbon upon an asbestos filter.

The Asbestos Filter is Prepared by stopping the neck of a funnel with a plug of glass-wool. Asbestos, which has been ignited in a current of air, is then broken up with water in a mortar, and is poured into the funnel. In this way a layer of felted asbestos fibres is formed, which will serve as a filter. Before the filter is used, water is poured into it and is drawn through by an aspirator as long as any fibres are carried through.

FIG. 74.

A special funnel may be made for the purpose of the filtration in the following way. A piece of combustion-tube, about 4 inches long and ¾ inch in internal diameter, is drawn out at one end until a small orifice only is left (fig. 74). It will be found convenient to introduce a platinum wire into the funnel, which serves for pushing out the asbestos, after the filtration, into the boat. The glass-wool and asbestos are then introduced in the way described above. The solution is filtered rapidly by means of the filter-pump (58).

If a small platinum tube is used instead of the glass tube described above, it may be pushed with its contents into the combustion-tube: the transference of the asbestos and carbon to the boat is thus saved.

Transfer the liquid and the carbon to the funnel containing the asbestos filter, and wash the filter until it is free from chloride. Then dry the filter in the steam-oven, and transfer the asbestos containing the carbon to a porcelain or platinum boat, and proceed to make a combustion such as is fully described in par. 653.

The boat is pushed into a combustion-tube, the front part of which contains about 6 inches of granulated copper oxide, and a silver coil to absorb any chlorine. The open end is fitted with a perforated cork, which carries a calcium chloride tube, to which is attached a weighed soda-lime tube. The calcium chloride tube absorbs any moisture which may be evolved, the soda-lime tube absorbs the carbon dioxide.

After the apparatus has been tested to ascertain that it is air-tight, the combustion-tube is laid in the furnace, and the copper oxide layer is heated to redness. A slow current of pure dry oxygen is then passed through the tube, and the heat is extended to the boat containing the carbon. After all the carbon is seen to be burnt off, the current of oxygen is allowed to pass for a short time to sweep over the carbon dioxide into the absorption tube. The soda-lime tube is then detached, and is weighed as soon as it is cold. From the weight of CO_2 thus found, the percentage of carbon in the iron may be calculated.

457. **Estimation of Graphite.**—Weigh out accurately about 3 grams of the iron, and heat it gently with hydrochloric acid diluted with an equal volume of water. Collect the insoluble residue of impure carbon on an asbestos filter: wash it successively with hot water, potassium hydrate solution, alcohol, and ether.

Then dry the residue, and estimate the amount of graphite it contains by burning it in a stream of oxygen, and absorbing and weighing the carbon dioxide, as is described in the last paragraph.

For certain technical purposes, in which great accuracy is not required, the iron may be dissolved in hydrochloric acid, as is

described above; and the residue may be collected on a tared filter, then washed as before, and dried and weighed. It is then transferred to a platinum crucible, the filter-ash is added, and the carbon is burnt off, with the aid, if necessary, of a stream of oxygen (67).

Since a platinum crucible suffers by the long contact with the gas-flame which is necessary to burn off the graphite, the method of combustion described in 473 may be resorted to, using oxygen if necessary.

The loss of weight of the residue, after allowing for the weight of the filter and of the filter-ash respectively, gives approximately the weight of the graphite. The result thus obtained for graphite is usually about 20 per cent. too high, owing to the oxidation of the Fe. It should be corrected by multiplying it by the factor 0·8.

458. Estimation of Combined Carbon in Steel and in Wrought-iron by Eggertz's Method.—When metallic iron contains only a small proportion of carbon, its solution in nitric acid is usually brown. The depth of this colour increases as the percentage of combined carbon present in the iron increases. Hence by comparing the coloration of this solution, with that obtained by the solution of standard iron containing a known quantity of carbon, a very exact determination of carbon may be rapidly made.

In practice, nitric acid of 1·2 specific gravity is used. A series of standard samples of steel are first prepared, the amount of carbon in each of which has been accurately determined by the combustion method (456). As a rule, the standards should be prepared from the same kind of steel as that which is to be tested.

The process may be carried out as is described below, or by Stead's modified method (459).

For the estimation, weigh out accurately 0·2 gram of the sample to be tested, and the same weight of the standard steel, into two test-tubes. Dissolve these in the proper amount of nitric acid, which must be of 1·2 specific gravity, and be free from chlorine. If an insufficient amount of nitric acid is used, the solution is slightly darker in tint.

The proper quantity of nitric acid to be used for the solution of the sample may be ascertained from the following statement:—

Percentage of carbon present in steel.	Number of c.c. of nitric acid required for solution.
Less than 0·3 per cent.	3 c.c.
From 0·3 to 0·5 ,,	4 c.c.
,, 0·5 ,, 0·8 ,,	5 c.c.
,, 0·8 ,, 1·0 ,,	6 c.c.
Upwards of 1·0 ,,	7 c.c.

If no knowledge of the probable percentage of carbon is obtainable, 3 c.c. of the acid may be used. This quantity should be afterwards increased, if necessary, in a repetition of the process.

The test-tubes are heated in a water-bath, until all action ceases and the solution of the metal is complete: one hour will be the extreme time required. The tubes are then at once removed from the water-bath, and are cooled by being immersed in cold water.

Now pour the standard solution into a "carbon-tube." This is a glass tube, $\frac{1}{2}$ inch in diameter, and closed at one end; it is capable of holding 30 c.c., and is graduated into tenths of a c.c. Rinse out the test-tube with water, until the total volume of liquid is at least twice as great as that of the acid originally used. The volume of the standard solution should be some convenient multiple of tenths per cent. Thus, if the standard iron used contains 0·5 per cent. of carbon, and the solution is diluted until it measures 10 c.c., each c.c. of this liquid will correspond to 0·05 per cent. of carbon.

Next pour the solution of the sample under examination into a similar carbon-tube, and rinse out the test-tube with a small quantity of cold water. Compare the intensity of the colours of the two solutions, by looking across the tubes at a white surface.

If the colour of the sample-solution is the more intense, add water to it gradually until the colours exactly correspond. Now read the volume of this solution in cubic centimetres.

The percentage of carbon will be found by multiplying

the number of c.c. of liquid in the tube by the carbon-value of 1 c.c. of the standard solution.

Thus, if 11 c.c. of the sample-solution gave the same colour-intensity as 10 c.c. of the standard solution, each c.c. of which corresponds to 0·05 per cent. of carbon, then the percentage of carbon in the sample = $11 \times 0{\cdot}05 = 0{\cdot}55$.

Instead of diluting the sample-solution until its intensity corresponds with that of the standard solution, a graduated series of standard solutions may be employed. These are contained in sealed tubes, and successively differ by a fixed amount of carbon. Since, however, these colours are liable to fade, the method described above is more trustworthy.

459. Stead's Modified Process for determining Combined Carbon.—It is found that the colour which is due to the solution of the carbon is interfered with by that of the iron nitrate present in the liquid. This interference is prevented by precipitating the iron from the solution by the addition of sodium hydrate solution in excess, and then removing it by filtration. The colour due to the carbon is more intense in the alkaline filtrate than it was in the original acid solution.

One gram of the iron is dissolved by heating it in a water-bath with 12 c.c. of nitric acid, of 1·2 specific gravity. The standard iron is treated in a similar way. Each solution is then well mixed with 30 c.c. of hot water and with 13 c.c. of solution of sodium hydrate of 1·27 specific gravity. The liquids are then diluted to 60 c.c. and are well shaken, and after standing for ten minutes in a warm place they are filtered through dry filters.

The two filtrates are poured into two graduated tubes, and the intensity of their colour is compared by looking down the tubes upon a white surface. The lengths of the columns are then adjusted so as to give equal colour intensity. The quantities of carbon present are inversely as the lengths of the liquid columns.

Thus if the columns of liquid measure respectively 80 mm. and 100 mm., the latter corresponding to the standard iron containing 0·4 per cent. of iron; then the percentage of carbon in the iron sample $= 0{\cdot}4 \times \frac{100}{80} = 0{\cdot}5$.

It is found that the colour which is given by iron containing a low percentage of carbon, differs from that given by iron containing a high percentage. Hence it is necessary to prepare separate standard solutions for the two classes of iron.

460. The Percentage of Free Carbon may be found by subtracting the percentage of combined carbon from the percentage of total carbon.

461. Estimation of Sulphur.—Two methods are in common use.

(1) The sulphur is converted into hydrogen sulphide and is weighed in a suitable form (**462**). This process is applicable to steel. If it is applied to cast-iron some of the sulphur often fails to be converted into hydrogen sulphide.

(2) The sulphur is converted into sulphuric acid, and is weighed as barium sulphate (**463**). This method gives more accurate results than the first, and is of general application.

462. *Estimation of Sulphur by conversion into Hydrogen Sulphide.*—Weigh out about 10 grams of the iron into a 10-oz. conical flask. Fit into the neck of the flask a doubly perforated rubber stopper, which has been previously boiled with sodium hydrate solution to extract the sulphur from the rubber.

Through one hole in this stopper push a thistle-funnel, which must nearly touch the bottom of the flask. Into the other hole fit a tube bent twice at right angles, the shorter end of which just passes through the cork, while the other end passes into a tall narrow cylinder containing a dilute solution of cadmium chloride or sulphate.

As a further precaution, the gas which is evolved may be made to pass through a second similar cylinder, connected

with the first by means of a cork and bent tube; this, however, is rarely necessary.

Dilute hydrochloric acid is poured upon the iron through the funnel, and the contents of the flask are finally boiled to expel dissolved hydrogen sulphide gas. The precipitated cadmium sulphide is washed on a tared filter, which has been previously dried at 100° C., and is dried at 100° C. and weighed (155).

If this method is applied to cast-iron, it is always necessary to filter off and wash the undissolved residue in the flask; it is then dried, and the sulphur which remains in it is estimated by the process described in paragraph 104.

If the amount of sulphur to be estimated is very small, the hydrogen sulphide may be received in bromine water acidified with hydrochloric acid. The excess of bromine is expelled by boiling, and the sulphur is then precipitated and estimated as $BaSO_4$ (96).

463. *Estimation of Sulphur as* $BaSO_4$.—Weigh accurately 5 grams of the iron, dissolve this in aqua regia, and evaporate the solution to dryness at a moderate heat on the iron-plate or air-bath (50, d) to get rid of the nitric acid. Moisten the residue with hydrochloric acid, add water, heat, and filter. This residue may be used for the estimation of silicon as is described in par. 464.

Dilute the filtrate slightly, and add an excess of barium chloride solution; allow the liquid to stand, and weigh the barium sulphate (96).

This method gives more accurate results than that described in par. 462, provided that care is taken to remove most of the free acid or to keep the volume of the liquid small, and to add a good excess of barium chloride solution.

464. **Estimation of Silicon.**—Dissolve from 3 to 5 grams of the iron in strong nitric acid, taking care to prevent loss by spirting if the action is violent.

As soon as the metal is completely dissolved, evaporate the solution to dryness. Decompose the carbonaceous matter by heating the residue to about 200° C. on the air-bath

(50, d), else the precipitation of the phosphate in the filtrate (465) will be incomplete. The addition of a little ammonium nitrate greatly promotes the destruction of the carbonaceous matter.

Dissolve the cold residue in hydrochloric acid, and evaporate this solution to dryness, in order to render the silica insoluble. Heat the residue with hydrochloric acid, and evaporate most of the acid. Then dilute with water, and filter off and wash the silica, taking care that the volume of the filtrate and washings does not exceed 100 c.c. Keep this filtrate for the estimation of phosphorus (465). Dry, ignite, and weigh the silica (386).

If the silica is coloured red by iron oxide, it must be digested with strong hydrochloric acid until it is perfectly white; it is then washed, dried, and ignited. The weight of pure silica should then be ascertained by treatment with pure hydrofluoric acid, as is directed in paragraph 172.

465. **Estimation of Phosphorus.** — The phosphorus is converted by the action of strong nitric acid into phosphate, and the phosphate is precipitated by molybdate solution.

The phosphorus is then either weighed in the form of phospho-molybdate (467), or as magnesium pyrophosphate (466).

466. *Estimation as* $Mg_2P_2O_7$.—Add to the filtrate from 464, which measures about 100 c.c., a large excess of ammonium molybdate solution (449). The volume of the molybdate solution added must be equal to at least twice that of the liquid. Allow the liquid to stand for several hours in a warm place, taking care that the temperature does not exceed 40° C., else arsenic may be precipitated.

Remove a small quantity of the clear liquid by a pipette; mix it with some more molybdate solution, and allow the liquid to stand in a warm place for some time. If any further precipitate is thus produced, this process must be repeated.

As soon as the precipitation is proved to be complete, filter

off the precipitate, and wash it with molybdate solution diluted with an equal volume of water; testing the washings with K_4FeCy_6 solution for Fe to ascertain when the washing is finished.

Dissolve the precipitate in 2 or 3 c.c. of strong ammonium hydrate solution; add strong hydrochloric acid until the liquid is nearly neutral: precipitate the phosphate by means of magnesia-mixture (**132**), and weigh it as $Mg_2P_2O_7$ (**131**).

467. *Estimation by Weighing as Phospho-molybdate.*—A modification of the above method consists in weighing the yellow phospho-molybdate precipitate itself. If this method is adopted, from 1 to 2 grams of the iron-sample should be treated as is directed in paragraph **464**.

After the silica has been filtered off, the volume of the filtrate is reduced by evaporation until a film forms upon the surface of the liquid. The phosphate in this solution is then precipitated with the molybdate solution as is directed above (**466**). The precipitate is washed with water containing 1 per cent. of HNO_3. It is then dried at 120° C. on a tared filter, and is weighed as $[(NH_4)_3.11MoO_3.PO_4]$, containing 1·63 per cent. of phosphorus.

468. Estimation of Manganese.—Weigh accurately about 2 grams of the iron sample, and dissolve it in nitric acid. Evaporate the solution to dryness, and heat the residue to 200° C. in the air-bath (**50, d**) to destroy carbonaceous matter. Dissolve the cold residue in hydrochloric acid, then dilute, and filter off insoluble matter.

Dilute this solution to about 500 c.c. with distilled water, and add ammonium carbonate solution, drop by drop, until the colour of the liquid becomes dark brown. Continue the addition of the ammonium carbonate solution very cautiously and with constant stirring, until the precipitate which is formed only just redissolves on stirring. Now add ammonium acetate solution and a little acetic acid, boil the solution for a few minutes, and filter it while hot by means of the funnel-jacket (fig. 54, p. 71).

Redissolve the precipitate in hydrochloric acid, add ammonium carbonate solution carefully, then acetate solution, and boil as before; then filter the hot liquid.

Mix the two filtrates, which will contain the manganese; evaporate if necessary, and allow the liquid to cool. To the cold solution add bromine-water until the solution is of a brown colour, and then add an excess of ammonium hydrate. Heat to boiling, filter off and wash the precipitate with hot water; then dry and ignite it, and weigh as Mn_3O_4.

Note.—This precipitate always contains some Ni or Co, which in *very* accurate estimations must be separated and weighed.

469. Estimation of Copper and Arsenic.—Weigh accurately from 5 to 10 grams of the iron, and dissolve it in nitric acid. Evaporate the solution to dryness two or three times on the water-bath with hydrochloric acid. Dissolve the residue in water, reduce the iron to the ferrous state by means of ammonium bisulphite (**262**), and pass hydrogen sulphide gas into the solution to saturation. Filter off the precipitate, which may contain CuS, As_2S_3, S, and possibly Sb_2S_3; and separate and estimate these substances as is described in paragraph **422**.

A trace of copper is more readily estimated volumetrically (**554**).

Proximate Analysis of Coal and Coke.

470. The chemical examination of coal ordinarily comprises the estimation of moisture, ash, sulphur, volatile matter, coke, and calorific power. The results thus obtained will usually enable a judgment to be formed of the quality of the coal from a chemical standpoint.

471. Estimation of Moisture.—Powder about 2 grams of the coal very finely, weigh the powder between two watch-glasses (**16**), and heat it in the steam-oven. Remove the coal every two hours, allow it to cool in the desiccator, and weigh it. Since the weight increases after a time by oxidation, no constant weight will be obtained. The lowest

weight, which is noted during the series of weighings, should be taken.

472. Estimation of Volatile Matter and Coke.—Two methods (a, b) for estimating the volatile matter and coke are described below.

(a). Spread out 2 grams of the finely-powdered coal in an even layer in the bottom of a weighed platinum crucible. Cover the crucible with the lid, and place it on a pipe-clay triangle, over a powerful Bunsen-flame. In order that comparable results may be obtained in different estimations, the length of the flame and the position of the crucible in it must be the same in all experiments.

As soon as the flame of the gases, issuing from beneath the lid, ceases, continue the heating for one minute longer. Then remove the gas-flame, allow the crucible to cool in the desiccator, and weigh it without the lid as soon as possible.

(b). Weigh out accurately from 10 to 20 grams of the coarsely-powdered coal into a weighed capacious porcelain crucible provided with a lid. The crucible should not be more than half filled with the coal. Place this crucible in a clay crucible, and surround it completely with coarsely-powdered charcoal. Cover the clay crucible with its lid, place it in a wind- or gas-furnace, and keep it at a red-heat for one hour. Remove the porcelain crucible when it is cold and weigh it. The loss of weight, which it has sustained, represents the volatile matter of the coal. The residue consists of the coke, including the ash.

An examination of the coke obtained by this method will indicate whether the original coal is a caking, sintering, or non-caking coal.

473. Estimation of Ash.—Weigh out accurately about 2 grams of the powdered coal, or of the coke from **472**, into a weighed porcelain-boat about 4 inches long and $\frac{3}{4}$ inch across. A piece of platinum-foil, which has been shaped upon a piece of glass rod, forms a good substitute for the porcelain-boat.

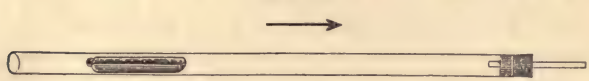
Push the boat containing the coal into a piece of combustion tubing, about 1 inch in diameter (fig. 75). Heat the tube and boat to redness in a gas-furnace, while a gentle current of air is drawn through the combustion-tube by means of an aspirator (58, 140).

Take care that the temperature does not become sufficiently high to soften the glass, else the boat and tube may stick together. As soon as the combustible matter is entirely removed, allow the tube to cool; then withdraw the boat, and weigh it. By this method a "clean" ash is obtained in a short time.

Reserve the ash for the determination of the sulphate which it contains.

474. **Estimation of Sulphur.**—It is usually necessary to ascertain the amount of sulphur present in the volatile matter, the sulphur contained in the coke, and the sulphur left as

FIG. 75.



sulphate in the ash. For this purpose the determinations of the total sulphur (475), of the sulphur in the ash (476), and of the volatile sulphur in the coke (477) are necessary.

The amount of sulphur present in the volatile matter is found by adding the amount of sulphur found in the ash to the amount evolved by burning the coke, and then subtracting this from the total sulphur.

475. **Total Sulphur, Nakamura's Method.**—Weigh out accurately about 1·5 grams of the *very finely-powdered* coal (*Note*), and mix it with four times its weight of finely-powdered dry sodium carbonate. This mixture is effected by adding the sodium carbonate gradually to the coal contained in a platinum crucible or capsule, and stirring constantly with a dry glass rod.

Now partially cover the crucible with its lid, and heat it

gently at first, so as not to volatilise the hydrocarbons. During the heating either no smell, or only a faint aromatic smell should be observed.

Use a spirit-lamp in preference to a Bunsen-burner, in order to avoid the possible introduction of sulphur from the coal-gas.

Keep the crucible at a low temperature for some time, then gradually raise the temperature nearly to visible redness; and continue the heating until the dark grey surface of the mixture fades to a faint grey. No smoke or odorous gases should escape during any part of this process.

As soon as the colour of the surface of the mixture is only faintly grey, raise the temperature to a dull red-heat, and maintain this temperature for about 50 minutes. At the end of this time the mass will have become almost perfectly white, owing to the complete combustion of the coal; the tint will, however, be red if iron is present in the coal.

Treat the cool mass with water, and filter the solution. Boil the filtrate, after adding a few drops of bromine and acidifying with HCl, and continue boiling until the bromine is removed. Then determine the sulphate as $BaSO_4$ (96).

Note.—In order to secure the complete oxidation of the coal by the above treatment, it is most important that it should be powdered as finely as possible.

If the solid mixture is stirred during the heating, the oxidation of the coal is much impeded.

476. **Sulphur in the Ash.**—The ash obtained in 473 is treated with water, containing a little hydrochloric acid; the solution is filtered, and the residue is washed. The sulphate is determined in the filtrate and washings as $BaSO_4$ (96).

477. **Volatile Sulphur in the Coke.**—The sulphur which is converted into sulphur dioxide, when the coke is burnt in the air, is determined as follows.

A quantity of coke (472), representing a known quantity of coal, is roasted in a porcelain-boat, or on platinum-foil, in

a current of air (473). The gaseous products are drawn by an aspirator through 10 c.c. of standard solution of iodine (276) placed in a bulbed U-tube (fig. 72, p. 208). The following reaction will take place:—

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI.$$

The amount of free iodine remaining in solution is determined by standard sodium thiosulphate solution (279), and the amount of iodine which has been acted upon by the SO_2 is obtained by difference. From this the weight of the S may be calculated.

478. Estimation of Calorific Power.—The calorific power of fuel is the number of heat-units which are obtained by the combustion of unit weight of the fuel in oxygen. One heat-unit or "calorie" is the amount of heat required to raise the temperature of 1 gram of water 1 degree Centigrade.

In the method described below, the fuel is first mixed with some substance which is capable of yielding oxygen, such as potassium nitrate or potassium chlorate. The mixture is then kindled, and the products of combustion are passed through a known weight of water. The increase of temperature thus produced in the water is noted as soon as the combustion has ceased.

The weight of water in grams, multiplied by the rise of temperature in Centigrade degrees, will then give the number of units of heat evolved by the combustion of the fuel. This number, after it has been corrected for the heat absorbed by the apparatus, gives the calorific power of the fuel.

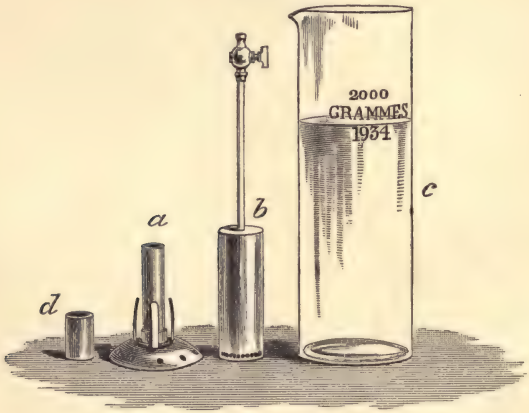
479. Estimation by Lewis Thompson's Calorimeter.—The calorific power of coal may be estimated on the above principle by Lewis Thompson's calorimeter. The results furnished by this apparatus are only approximately accurato, but they suffice for the commercial valuation of coal.

The calorimeter apparatus is shown in fig. 76. It comprises a glass cylinder (*c*), which is capable of holding 2000 grams of water when it is filled up to the etched mark: and a suitable metal vessel and tube in which the fuel can be burnt.

Before using the calorimeter, fill it to the mark with water at about 15°·5 C., and take the temperature of the water carefully by means of a delicate thermometer.

Weigh out accurately 2 grams of the finely-powdered and sifted coal. Mix this intimately with ten times its weight of

FIG. 76.



a mixture of one part of potassium nitrate and three parts of potassium chlorate, which has been previously well dried in the steam-oven. Then try to kindle the mixture. If it does not burn steadily, the amount of oxidising mixture must be varied.

As soon as a mixture has been prepared which burns steadily, transfer a similar mixture to the copper tube (*a*), seen on the left in the figure, and gently tap the tube on the bench so as to cause the mass to settle down. The broader tube (*d*) is intended for a mixture which does not burn readily.

When all the powder has been transferred to the tube, insert a little piece of fuse, which is made by steeping thin cotton-wick in nitre solution and drying it. Now place the tube in the brass clips attached to the brass disc. Light the fuse, rapidly push on the cover (*b*), taking care that the stopcock is closed, and immerse the tube in the water contained in the glass cylinder.

The cover (*b*) consists of a copper cylinder connected with a narrow copper tube. The cylinder prevents the water from coming into contact with the mixture. It is perforated at the bottom so as to allow the products of combustion to escape. The narrow tube attached to the cylinder is provided with a stopcock, so that the water can be admitted into the cylinder and tube at the end of the combustion.

The whole metal apparatus is allowed to remain immersed in the water for a few seconds, after the gaseous products of combustion have forced their way through the holes at the base of the copper cylinder, and have passed up through the water into the air. The heated products and metal will then have transferred their heat to the water.

The stopcock is now opened, so as to admit water to the interior of the metal apparatus. The metal apparatus is then alternately raised and lowered several times so as to mix the water thoroughly, and the temperature of the water is once more taken.

Since 2 grams of coal were used, and the glass cylinder contained 2000 grams of water, the number of Centigrade degrees by which the water has increased in temperature is added to the amount of heat absorbed by the apparatus, and this number, when it is multiplied by 1000, will give the number of units of heat evolved by the fuel. Ten per cent. of the total rise of temperature observed, is usually taken as representing the amount of heat absorbed by the instrument.

In a particular estimation the following results were obtained. The initial temperature of the water was 16° C.; the final temperature of the water was 22°·7 C. The correction for the heat absorbed by the

apparatus amounts to 10 per cent. of the rise of temperature observed in the water. Therefore the calorific power $= (6{\cdot}7 + 0{\cdot}67)\ 1000 = 7370$ calories, or heat-units.

A second graduation will be seen on the glass cylinder at 1934. The cylinder may be filled with water up to this mark, and the temperatures may be taken in Fahrenheit degrees. The number, calculated as above from the results thus obtained, will represent the number of pounds of water which the burning of one pound of the coal will convert into steam. The calculation is based on the assumption that $\frac{1934}{2} = 967$ units of heat are required to convert the unit weight of water into steam.

For Results of Analysis of Coal, see Appendix (764).

Analysis of Superphosphate of Lime.

480. Most of the natural calcium phosphates, including the calcium phosphate present in bones, are insoluble in water. But when these substances are treated with sulphuric acid, the insoluble tri-calcium phosphate ($Ca_3P_2O_8$), which they contain, is converted into soluble mono-calcium phosphate, $CaH_4P_2O_8$. The treatment of these phosphates with sulphuric acid, which is performed on a large scale by manure manufacturers, produces the "superphosphate" of commerce.

"Superphosphate" consists essentially of mono-calcium phosphate; but it also contains varying proportions of the following substances, tri-calcium phosphate, calcium sulphate, and compounds of iron, aluminium, magnesium, and the alkali-metals. Organic matter is also usually present.

481. Estimation of Moisture.—Weigh out accurately about 2 grams of the superphosphate in the watch-glasses and clip, and heat it in the steam-oven until its weight is constant. The loss of weight represents the amount of moisture, or uncombined water.

482. Estimation of Combined Water.—The superphosphate, after having been dried as above (**481**), is transferred to the air-oven, and is heated to 160° C. until its weight is constant. The loss of weight represents the amount of combined water.

483. Extraction of the Portion which is Soluble in Water.—Weigh out 10 grams of the well-sampled, undried, superphosphate into a mortar. Add a little water, and mix the whole into a paste by gently stirring it with the pestle. Add more water, stir well, and allow the undissolved matter to settle; then decant the almost clear liquid into a flask. Treat the residue again with water, and once more decant. Repeat these operations twice, and finally transfer the undissolved residue to the flask. Allow the flask to stand for two hours, shaking it occasionally.

Now filter the liquid into a half-litre flask, and wash the undissolved residue on the filter with water, until the flask is filled up to the graduation. Reserve the residue in the filter for subsequent estimations (**488–490**), and proceed to use this "original solution" for the following estimations (**484–487**).

484. Estimation of Phosphates of Iron and Aluminium, and of Soluble Calcium Phosphate.—Transfer 250 c.c. of the above "original solution" to an evaporating dish, add a little sodium carbonate to neutralise the free acid, and then a few small crystals of potassium nitrate. Evaporate this liquid to dryness, and ignite the residue to remove the organic matter. As soon as the dish is cold, add hydrochloric acid and water. Add more acid and heat, if the liquid is not clear. Now add a slight excess of ammonium hydrate solution, and then an excess of acetic acid. Filter off the aluminium and iron phosphates; and wash, dry, ignite, and weigh them.

Make up the filtrate to 250 c.c., and withdraw two successive portions of 50 c.c. each. Make duplicate determinations in them of the P_2O_5 by means of standard uranium nitrate solution, which has been standardised with calcium phosphate solution (**310**).

An alternative gravimetric method consists in precipitating the phosphate in 50 c.c. of the "original solution" with ammonium molybdate solution, and weighing it as magnesium pyrophosphate (466).

485. **Estimation of Calcium and Magnesium.**—Transfer 100 c.c. of the filtrate from 484 to a beaker; add excess of ammonium oxalate solution; filter off and wash the precipitate; and weigh the calcium either as carbonate or as oxide (110, 111).

The filtrate, which contains the magnesium, is rendered alkaline with ammonium hydrate, when the magnesium will probably precipitate; sodium phosphate solution is then added, and the liquid is allowed to stand. The precipitate of magnesium ammonium phosphate is ignited and is weighed as magnesium pyrophosphate, as is described in paragraph 130.

486. **Estimation of Organic Matter and Alkali-metals.**—Transfer 100 c.c. of the "original solution" (483) to an evaporating dish, and mix it with milk of lime until the liquid is just alkaline. Evaporate to dryness, and heat the residue in the air-oven at 160° C. until its weight is constant. Then ignite over a small Bunsen-flame until the dish ceases to lose in weight. The loss of weight gives the amount of soluble organic matter in the superphosphate.

Treat the residue with water, add a little more milk of lime, and heat for some time. Filter off the insoluble matter and wash it twice. Then precipitate the sulphate and the calcium from the filtrate and washings, by adding barium chloride, ammonium hydrate, ammonium carbonate, and ammonium oxalate solutions in the order named. Filter, convert the alkali-metals in the filtrate into chlorides by adding hydrochloric acid, and estimate them as is described in paragraphs 358, 359.

487. **Estimation of Sulphate.**—Heat 100 c.c. of the "original solution" (483) to boiling, add a few drops of hydrochloric acid, and precipitate with barium chloride solution. Weigh the barium sulphate (96).

488. Estimation of Insoluble Organic Matter.—The residue left on the filter (483) will contain the organic matter, gangue, and undissolved phosphate and sulphate. Dry the residue in the steam-oven, transfer it as completely as possible to a platinum crucible, and weigh. Then ignite the crucible until all the organic matter has been destroyed. The loss of weight will give the amount of organic matter.

489. Estimation of Silicious Matter.—Heat the ignited precipitate (488) with hydrochloric acid, to extract the portion which is soluble in acid. Filter off, wash, ignite, and weigh the residue, which consists of gangue or silicious matter.

490. Estimation of Iron, Aluminium, Phosphate, Calcium, Magnesium, and Sulphate.—Make up the filtrate from 489 to 250 c.c., and estimate its dissolved matter exactly as is described in paragraphs 353–357 and 360.

491. Estimation of Nitrogenous Matter.—Superphosphates are occasionally mixed with nitrogenous manures and ammoniacal salts.

The total nitrogen in the superphosphate may be determined in 2 grams of the substance by the soda-lime method, or by Kjeldahl's method (663) if nitrates are absent.

The ammonia may be determined by mixing 2 grams of the substance with sufficient water, then adding sodium hydrate, or magnesia if much nitrogenous matter is present, and distilling. The ammonia gas is received in standard acid, which is titrated as is described in paragraph 139.

For the Results of an Analysis, see the Appendix (765).

Analysis of Mineral Phosphates and Bone-Manures.

492. The above process for the analysis of a superphosphate is applicable to the analysis of other mineral phosphates. Since, however, these contain little or no

matter soluble in water, the treatment with water may be omitted, and the phosphate may be at once treated with acid. Any carbonate present is estimated as is described in paragraphs **140–149**.

For Results of Analyses, see Appendix (**766, 767**).

Estimation of the Total P_2O_5 in "Basic Slag," Mineral Phosphates and Superphosphates.

493. For the estimation, 10 grams of the "Thomas' slag" are heated with 50 c.c. of strong H_2SO_4 for fifteen minutes, to a temperature at which white fumes appear. The cold liquid is then diluted to 500 c.c. and filtered.

50 c.c. of the filtrate are then mixed with 20 c.c. of citric acid solution, containing 500 grams of acid per litre; and the liquid is nearly neutralised with ammonia solution, containing one-tenth its volume of the strongest ammonia (sp. gr. 0·88).

The solution is then precipitated by magnesia mixture (**132**), and mixed with one-third its volume of the above ammonia solution.

The precipitate is weighed as $Mg_2P_2O_7$ (**131**).

For Results of Analyses, see Appendix (**765–769**).

Analysis of Guano.

494. Since guano gives off ammonia when it is heated to 100° C., its moisture cannot be estimated in the ordinary way. About 4 grams are weighed into a bent glass tube (**154**), which is immersed in an oil-bath heated to 120° C.

One end of the tube is connected with a wash-bottle, containing a known volume of normal acid; and a current of air is aspirated through the tube and wash-bottle. The ammonia gas, which is given off during the heating, is thus drawn into and absorbed by the acid in the wash-bottle. After the heating is stopped, the ammonia is estimated

by titrating the free acid with standard sodium hydrate solution.

The loss of weight of the guano gives the water + ammonia, hence the water may be calculated by difference. The dried substance is then ignited strongly in the air, to ascertain the amount of organic matter.

The residue is treated with HCl, and the estimations described in paragraphs 484–487 are made in the solution.

For Results of Analysis, see Appendix (768).

DRY ASSAY FOR LEAD, FOR SILVER, AND FOR GOLD.

Dry Assay of Lead Ores.

The chief ore of lead is galena, PbS. It always contains more or less silver, so that in an assay of this ore silver is invariably estimated.

495. Dry Assay of Galena for Lead. — The lead is reduced to the metallic state by means of a suitable flux in an iron crucible.

For the estimation weigh out 30 grams of the finely-powdered ore, and mix this with 30 grams of dry sodium carbonate and 30 grams of crude tartar. Transfer the mixture to a wrought-iron crucible, which has been previously heated to dull redness in a wind-furnace, and cover with a sprinkling of borax. If the crucible has been previously used, scrape off the scale from the interior before introducing the mixture. Put on the lid, place the crucible in the wind-furnace, and surround and cover it with coke.

Heat moderately for about twenty minutes, taking care not to let the temperature rise too high. Take the crucible out of the furnace, and scrape down any slag adhering to the sides with an iron stirrer. Tap the crucible gently, and

pour the melted mass into a smooth conical iron mould. When the whole has become cold, the metal will be found at the bottom of the mould in the form of a button. Break off the slag with a hammer, and beat the lead until all the slag is detached. Finally wash, dry, and weigh the lead button.

After the fusion the interior of the crucible should be smooth, and should have no globules of lead or of partly fused portions of slag adhering to the sides. The slag should be homogeneous, and should contain no particles of lead or undecomposed galena.

A wrought-iron crucible will serve for from 10 to 20 assays.

In order to obtain good results, several assays must be made on the same ore.

496. Assay of Oxide and of Carbonate of Lead.—The assay of oxidised ores, free from sulphur, arsenic, and phosphorus, is readily made by means of charcoal or tartar.

Weigh out 30 grams of the finely-powdered ore: mix this with 10 grams of sodium carbonate and of tartar, and about 1·5 grams of finely-powdered charcoal. Place the mixture in a small covered clay crucible (Battersea round), fuse in the wind-furnace at a moderate heat, and pour. Detach the lead button from the slag, clean and weigh it, as is described in **495**.

Assay of Lead for Silver.

497. The button of lead (**495**) containing the silver is melted on a shallow vessel made of bone-ash, known as a cupel, and is heated in a muffle-furnace. A muffle-furnace is one into which the products of combustion do not enter, and in which the current of air can be regulated.

The button melts and the lead is converted into oxide, which partly volatilises and is partly absorbed by the cupel.

The silver is left as a small globule, which may be detached and weighed.

498. Preparation of Bone-ash Cupels. — Cupels may either be purchased, or they may be prepared as follows.

Moisten some finely-powdered bone-ash with water, and work it in a mortar, until it just holds together when it is pressed, without soiling the hands.

The apparatus in which the cupels are made consists essentially of a mould in which the bone-ash is placed, and a plug which produces the desired cavity by compression.

Place the moistened bone-ash in the mould, place upon this the plug, and tap it sharply with a hammer several times. Detach the cupel, and dry it in the steam-oven. The cupel is then ready for use.

499. The Process of Cupellation.—Place one of the cupels in the hot muffle, and heat it to redness for five minutes, so as to drive off all moisture.

Lay the button of lead (**495**) on the cold cupel by means of the assay-tongs, and close the muffle-door. At the start take care that the temperature is a bright red-heat. A black crust will form on the surface of the lead, which in a short time disappears, and leaves the button brighter than the cupel. If this "clearing" does not take place, add a little charcoal, and raise the temperature of the muffle. If this is not successful, start afresh with a higher temperature.

As soon as the button is "clear," diminish the draught of the furnace, and allow a little air to enter by the muffle-door. Lower the temperature somewhat, since the temperature at starting is higher than is needed during the oxidation of the lead. If the temperature is too high, loss of silver by volatilisation will occur. At the finish again raise the temperature by closing the muffle-door and increasing the draught.

The final stage is easily recognised, since the thin layer of oxide will be reduced to a film which presents iridescent colours, and these suddenly disappear when the operation

is finished. The globule of silver then suddenly glows and solidifies.

Remove the cupel from the muffle, and allow it to cool. Detach the button, and hammer it out on a small anvil, and finally clean it with a hard brush. Weigh the button carefully on a very delicate balance, and calculate the weight of silver present in ounces per ton of lead.

Dry Assay of Gold Quartz.

500. Since the amount of gold in gold-ores rarely exceeds 2 oz. to the ton, and is usually much less, it is necessary to extract the metal with great care. The process is divided into three parts.

(1) The ore is heated with lead oxide and a flux. The lead, which is thus produced, extracts the gold and silver from the ore.
(2) The lead button is cupelled, and the silver and gold are left on the cupel.
(3) The gold is "parted" from the silver by dissolving out the latter with nitric acid.

501. Concentration of the Gold.—Powder the ore and pass it through the finest brass-wire sieve (35). Weigh out 50 grams, or, if the ore is a very poor one, 100 grams, and mix this intimately with the following flux:—

Red lead, ...	40 grams
Anhydrous sodium carbonate, .	100 ,,
Borax, ...	25 ,,
Flour, ...	4·5 ,,

Transfer the mixture to a smooth fire-clay crucible, cover it with the lid, and heat it in a wind-furnace. The heat at first must not be too great, but must be raised considerably before pouring. Pour into a conical iron mould, which has

been previously warmed. When the mass is cold, detach and clean the lead button. The slag should be glass-like, and should separate easily from the metal; it must contain no particles of lead.

502. Cupellation.—The lead button is now cupelled (499), a high temperature being used, so as to separate the copper completely. A high temperature may be safely used, since gold is much less volatile than silver. The button of gold and silver is then cleaned and weighed. If it shows a yellow colour it will contain more than 50 per cent. of gold.

503. Parting.—The process of "parting" consists in dissolving out the silver from the gold by means of nitric acid.

If the gold does not exceed 30 per cent. of the weight of the button, the whole of the silver will dissolve. If too much silver is present, the gold will be left as a powder which is difficult to manipulate. The most convenient proportions are 2·5 parts of silver to 1 part of gold.

If the gold does not exceed 30 per cent., flatten out the button by careful hammering. If the button is large, anneal it occasionally by heating it to redness on charcoal in the blowpipe-flame. Finally anneal the flattened button, in any case, before parting.

Heat a little strong nitric acid, diluted with three times its volume of water, nearly to boiling; and drop into it the weighed button. Keep the liquid at this temperature for ten minutes; pour off the acid, and heat the button with nitric acid diluted with an equal volume of water. Boil for several minutes. Pour off the acid, and wash the residue with distilled water.

Pour off the water, and fill up the tube with water. Cover the open end with a small porcelain crucible, and invert both tube and crucible. The gold will settle down to the bottom of the crucible. Drain off the water from the crucible. Dry the gold, and ignite it until it changes from a dark red to a yellow colour. Cool the gold, transfer it to

a watch-glass, and weigh it accurately. Calculate the weight of gold as ounces per ton.

If the button contains more than 30 per cent. of gold before "parting," it will retain silver. In such a case sufficient silver is added to raise the proportions to $2\frac{1}{2}$ parts of silver to 1 part of gold, and the parting is repeated with this alloy.

If the gold weighs only 2 or 3 milligrams, the requisite quantity of silver may be alloyed with it by simple fusion on charcoal before the blowpipe.

If the amount of gold exceeds a few milligrams, weigh out the required amount of silver, wrap the silver and gold together in 1 gram of sheet-lead (*Note*), and cupel. Flatten, anneal, and "part" the gold button. The gold will now be free from silver, and may be weighed; its weight is calculated as ounces per ton.

Note.—The lead which is used for this purpose must either be free from silver, or the amount of silver present in it must have been previously ascertained. The silver can be estimated by cupellation (499); but if it is very small in amount it must be determined as chloride by the process described in par. 413.

Example.—50 grams of ore were fused with flux; the button obtained was yellow, and therefore required cupelling with silver and lead. A button of "fine" metal weighing 6 milligrams was obtained; and the weight of gold found after parting was 1 milligram.

Hence the percentage weight of gold = 0·002,

$\therefore$ the weight of gold per ton of ore $= 0{\cdot}002 \times \frac{980}{3} = \underline{0{\cdot}65 \text{ oz.}}$

From the above results, the weight of Ag in the button = 5 milligrams.
Subtracting the weight of Ag in the lead used, . 1·1 ,,

The weight of silver from the ore = 3·9 ,,

$\therefore$ the weight of silver per ton of ore = $\underline{2{\cdot}54 \text{ oz.}}$

SECTION II.

WATER ANALYSIS.

520. Introductory Remarks.—The chemical examination of water is usually undertaken in order to ascertain the suitability of the water for drinking, or for technical purposes.

If the fitness of a particular water-supply for the purposes of washing or raising steam is to be ascertained, the examination may be restricted to certain determinations of its mineral constituents, such as total solid residue, permanent and temporary hardness, and acidity.

If, however, the suitability of the water for drinking purposes is to be determined, it often becomes necessary to estimate the amount of certain substances which are hurtful to health. Some of these are of a mineral character, such as lead salts. But commonly the most serious and dangerous contamination to be anticipated is that arising from drainage or sewage. The animal refuse, introduced in this form, is frequently indicated by the presence of an abnormal proportion of ammonium compounds, of chlorides, or of nitrites or nitrates in the water. These indications are usually valuable, but they are only of importance when no other source of these substances is possible.

The detection of more recent sewage contamination in the form of organic matter, involves the application of certain special processes. The most accurate and trustworthy of these processes is that of combustion introduced by Frankland and Armstrong. By this process the absolute amounts of carbon and nitrogen, constituting the organic matter in

the residue obtained by evaporation of the water, are determined: and from the absolute and relative amounts of these elements the existence and extent of recent sewage contamination can be readily inferred.

This process, however, involves the use of costly special apparatus, and also requires a somewhat considerable expenditure of time. Hence other processes for estimating organic matter in water, which are both simple and expeditious, have been more generally adopted by analysts. These processes are described in the text, and the student is referred to *Frankland's Water Analysis*, or to the description of this process in *Sutton's Volumetric Analysis*, for an account of Frankland's method.

Collection and Inspection of the Sample.

521. Collection of the Sample of Water.—The sample of water is most conveniently collected and stored in Winchester quart-bottles. These bottles are commonly made of blue glass, and are usually provided with accurately fitting stoppers. Each bottle holds about 2400 c.c. For an ordinary analysis, two Winchester quart-bottles filled with the water will be found sufficient.

Before the bottles are used for the water-sample, they should be well washed out with water, and then allowed to drain in an inverted position. Bottles which have been used for acids should be preferred, since they are most readily cleansed.

The use of stoneware bottles and of corks in storing water-samples is to be condemned.

Before the bottles are filled, they should be rinsed out two or three times with the water. When the water is to be collected from a river or spring, the bottles should be totally immersed in the water, and filled up to within half an inch of the bottom of the stopper. If the water is to be taken from a pump or tap, several gallons should be allowed to flow

away before the sample is taken. A sample of a town supply should be drawn direct from the street-mains, and not from a storage cistern.

The stopper should be inserted as soon as the bottle has been filled. It should be held in its seat by drawing down tightly over it a piece of sheet rubber, or clean calico or linen rag, the edges of which are firmly tied round just beneath the projecting edge of the neck with string or with thin copper binding-wire. The fastening should be sealed with sealing-wax. No lute or other material, which might find its way into the bottle when the stopper is removed, must be employed.

Samples of water should be stored in a cold, dark cellar.

522. Order of Work.—In carrying out the following estimations, the order in which they are to be started should be carefully considered, so as to economise time as far as possible. Experience has shown that if they are undertaken in the order in which they are described in the text, this end will generally be best secured.

Ammonia and organic matter should be determined as soon as possible after the collection of the sample, and immediately after the bottle has been opened, since they often suffer rapid change when the water is kept or is exposed to the air. The water in the bottle should always be shaken up before pouring off any portion for analysis, in order to keep it uniform in composition.

523. The Colour of the Water is seen by pouring it into a tall narrow cylinder of white glass, and looking down the cylinder upon a white surface. The tint should be compared with that of a sample of pure water. The cylinder, or tube, in which this test is made, should be about 2 feet in length.

The Taste and Smell of the water are usually observed after it has been gently heated.

Examination of Suspended Matter.

524. Chemical Examination of the Suspended Matter.—The presence of suspended matter in water is usually due to imperfect filtration, but may be due to the action of the water on lead (555), and to other causes. Unless the water is distinctly turbid, it is not usual to filter it before it is analysed. If, however, an appreciable amount of suspended matter is present, its amount may be estimated and the water at the same time rendered clear, in the following way.

Pour several litres of distilled water, free from ammonia, through a 6-inch filter-paper, with known weight of ash (64). This will dissolve out any ammonia present in the paper. Ascertain that the water, which passes through, has ceased to dissolve out any ammonia, by adding to the last portion of it 2 c.c. of Nessler-solution: this must remain colourless after standing for five minutes (530). Now dry the filter in the air-oven at 110° C., until its weight is constant (40).

Then place the filter in a funnel. Shake up the water for analysis in the bottle, and pour a measured quantity—say 2 litres—of the water through the filter, receiving the water in a clean dry Winchester quart-bottle. Remove the funnel from the bottle, wash the residue with distilled water, and dry it at 110° C. until its weight is constant.

The increase of weight of the filter gives the total suspended matter in the 2 litres of the water. Calculate the weight of dry suspended matter in parts per 100,000, by multiplying this weight by 50.

Now burn off the organic matter from the residue, and incinerate the filter in a platinum crucible (74). If the suspended matter is small in amount and adheres to the filter, the filter may be cut up into strips with a clean pair of scissors, and incinerated in the platinum crucible. As soon as all the carbon has been burnt away, recarbonate the residue by adding a few drops of ammonium carbonate solution; then ignite it again at a low temperature, and weigh it when it is cold.

This weight, less that of the filter-ash, gives the weight of inorganic suspended matter. Calculate from this the weight in parts per 100,000. The difference between this number and the one previously obtained for the total suspended matter, will give the amount of organic suspended matter.

525. Microscopic Examination of the Suspended Matter.—It is advisable to examine the suspended matter under the microscope. For this purpose allow the water to remain in a tall cylinder for several hours, until the suspended matter has been deposited. Carefully pour off the clear supernatant water as completely as possible; transfer a drop of the residual liquid to a glass slide, and examine it with a one-sixth objective. Take especial care to examine for fibres of wool, hair, muscular tissue, or any kind of animal matter which would be indicative of sewage. The presence of organisms should be carefully looked for. Chlorophyll granules and cells indicate vegetable matter.

Estimation of Total Dissolved Solids.

526. Rinse a clean platinum or porcelain evaporating dish with distilled water, and dry it in the steam-oven. Then allow it to cool, and weigh it accurately. Place the dish upon a glass ring on the water-bath, or on a beaker of suitable size placed on a tripod stand (**49**). The bath or beaker should be about two-thirds filled with water. A few small pieces of paper, thrown into the water in the beaker, will prevent the water from bumping while it is boiling.

Measure out 500 c.c. of the water into a gaduated *delivering* flask (**208**), and fill the dish to within half an inch from its edge with the water. As the liquid evaporates, keep filling in the water, until the whole of it has been transferred to the dish. When all the water has evaporated, cleanse and dry the outside of the dish, then place it in the steam-oven, and heat it until its weight is constant.

Since the residue in the dish is often very hygroscopic, the

weighing must be performed rapidly as soon as the dish is cold. It is advisable to cover the dish during the weighing with a plate of mica, which has been weighed with the empty dish.

The residue should be reserved in the dish for the estimation of the nitrate (541).

For Interpretation of the Results see par. 562.

Estimation of Ammonia.

527. All processes connected with this estimation must be conducted in a room which contains no ammonium salts or other sources of ammonia.

The estimation should be made as soon as possible after the collection of the sample, and immediately after the opening of the bottle.

The process depends upon the fact that, when the water is boiled with a little sodium carbonate, the whole of the ammonia, which is present in the water in a free or combined state, passes off in the first portion of the steam. The amount of ammonia in the distillate can then be estimated by the addition of Nessler-solution.

This solution gives a yellow or brown coloration with ammonia or ammonium salts, the intensity of the colour increasing with the proportion of ammonia present. The quantity of ammonia can therefore be accurately estimated, by comparing the colour with that given by the same quantity of the Nessler-solution, when it is added to the same volume of pure water containing a known amount of ammonium chloride.

The following requisites (528–533) must be provided for this estimation.

528. **Nessler Solution.**—Dissolve 62·5 grams of potassium iodide in about 250 c.c. of distilled water. Reserve about 10 c.c. of this solution. Add gradually to the main portion a cold saturated solution of mercuric chloride, until a permanent precipitate remains after thorough mixture. Now

cautiously add the reserved portion, until only a slight precipitate remains. Next dissolve 150 grams of caustic potash in 150 c.c. of water; allow the solution to cool, and add it to the above solution. Then add saturated solution of mercuric chloride until a permanent yellow precipitate is produced. Dilute this liquid to 1 litre, and allow it to stand for a short time.

Keep this Nessler-solution in a bottle which is closed with a well-fitting rubber stopper, and decant a portion of the clear solution from time to time into a smaller bottle for use.

It will be found convenient to fit a perforated rubber cork into the neck of the small bottle. A glass tube, with 1 c.c. and 2 c.c. marks upon it, passes through this stopper, and serves to deliver the required quantity of the solution.

529. Standard Ammonium Chloride Solution.—Weigh out accurately 1·5735 grams of pure recrystallised ammonium chloride. Dissolve it in water, and make the solution up to 1 litre. This solution will be too strong for use, but it is of convenient strength for a stock solution. When the solution is required for use, dilute 100 c.c. to 1 litre with water. Each c.c. of the diluted solution corresponds to 0·00005 gram of NH_3.

530. Water Free from Ammonia.—Ordinary distilled water frequently contains sufficient ammonia to render it unfit for use in this estimation. In order to ascertain whether ammonia is present in it or not, a small glass cylinder (**531**) is nearly filled with the water to be tested; 2 c.c. of Nessler-solution (**528**) are added, and the liquids are well mixed by stirring. The cylinder is then placed on a white surface. If the water develops no yellow coloration after standing for five minutes, it is sufficiently pure for use.

If, however, a yellow or brown coloration appears, the water must be redistilled as follows. Pour the distilled water into a large flask (**532**), and add about a gram of recently-ignited *sodium carbonate crystals* (**533**). Connect a Liebig's condenser with the flask, and proceed to distil the water, rejecting the first portion of the distillate. Then collect the

distillate in a small glass cylinder (531) and test it with Nessler-solution as is described above.

As soon as the distillate ceases to give a coloration with Nessler-solution, collect it in a Winchester quart-bottle, and keep the bottle, tightly stoppered, in a room which contains no ammonium salts or other sources of ammonia.

Instead of adding sodium carbonate to the water to liberate the ammonia, the ammonia may be retained in the water during the process of distillation by the addition of a few drops of dilute sulphuric acid.

531. **The Glass Cylinder** which is used for this purpose should be made of perfectly colourless glass, and should be 6 inches in height and 1½ inches in diameter, with a capacity of 100 c.c.

532. **Distillation Flask.**—If the flask, which is used for the distillation, is fitted with a rubber cork, it frequently happens that the distillate is contaminated with ammonia for a long time. Some rubber corks render it impossible to obtain ammonia-free water.

A convenient flask, which does away with this source of trouble, is a round fractionating flask of not less than 2 litres capacity, with the ordinary side-tube fused upon the side of the neck (fig. 17, p. 26). Its neck is closed by a well-fitting glass-stopper, ground in by means of fine emery-powder and water. The side-tube is passed to a distance of about 4 inches down the inner tube of the condenser, and is of such diameter as to fit the tube precisely. By this arrangement, direct contact of the steam with rubber is prevented, and freedom from ammonia is insured.

533. **Sodium Carbonate Crystals** do not contain ammonium salts; whereas other forms of the carbonate frequently contain these salts owing to ammonium salts having been used in their manufacture. It is extremely difficult to remove this impurity by ignition.

534. **The Process of Estimating Ammonia.**—The following preliminary test is first made for the purpose of ascertaining the amount of water which should be used for the more exact determination of the ammonia.

50 c.c. of the water under examination are measured into a glass cylinder (531), and the cylinder is placed upon a white tile. 2 c.c. of Nessler-solution are added to the water, which is then well stirred and is allowed to stand for five minutes.

Now pour 50 c.c. of the distilled water free from ammonia (530) into a second cylinder, and add 0·1 c.c. of the *dilute* standard ammonium chloride solution (529).

If the intensity of colour in both cylinders is about the same, use half a litre of the water for the determination. If the coloration produced by the water-sample is less or greater than that of the standard, use a proportionate quantity of the water. It should be remembered that a coloration corresponding to that given by about 0·4 c.c. of the standard ammonium chloride solution can be most accurately matched in the determination.

(a). *Process of Distillation.*—Now adapt the distillation flask to the Liebig's condenser (532), and proceed to free the apparatus from ammonia as follows. Pour into the flask about 250 c.c. of water free from ammonia (530), and a gram of recently-ignited sodium carbonate crystals (533). Boil the liquid briskly by heating the flask with an Argand-burner (70), and allow *the steam* to pass through the whole apparatus for a few minutes. Then distil and condense the steam until about 50 c.c. of water has been collected in one of the glass cylinders (531), and test this for ammonia by adding 2 c.c. of the Nessler-solution (530). If any ammonia is found, continue the distillation into fresh cylinders, until no ammonia can be found in the last portion of the distillate by Nessler-solution. The apparatus is now free from ammonia.

Now pour the requisite quantity of the water under examination into the flask, and distil over three separate portions of about 50 c.c. each into three cylinders. Reserve these in the order in which they have been collected. Then allow the apparatus and its contents to stand by undisturbed for the subsequent determination of the "albuminoid ammonia" (535).

(b). *Process of "Nesslerising."*—Add to the contents of the second of the test-cylinders, which contain the distillate, 2 c.c. of Nessler-solution, stir well, and place the cylinder on a white tile. Now make a comparison-test by pouring into a clean empty cylinder 50 c.c. of ammonia-free water, and adding to it as much of the standard ammonium chloride solu-

tion from a burette, as will probably give with Nessler-solution the same colour as that produced in the test-cylinder. About 0·2 c.c. may be added for this purpose. Allow both the cylinders to stand for five minutes before their tints are compared.

If the correct intensity of colour is not obtained, throw away the contents of the comparison-cylinder, rinse it out with water; pour in another 50 c.c. of the ammonia-free distilled water, and add to it more or less of the ammonium chloride solution, as may be considered necessary. Now add 2 c.c. of Nessler-solution, and compare the colorations after the cylinder has stood for five minutes.

These operations are repeated, if necessary, until the colour in the test-cylinder matches that in the comparison-cylinder.

The addition of the ammonium chloride solution to the water must never *follow* that of the Nessler-solution, else the liquid will become turbid, and an accurate comparison of the colours will be impossible.

The distillate in the third cylinder may be tested in the same way with the Nessler-solution, but it will usually be found to contain no ammonia.

If the colour given by the second cylinder does not require more than 0·3 c.c. of ammonium chloride solution to match it, the first cylinder may be tested at once in the same way as the second.

If more than 0·3 c.c. of the ammonium chloride solution is required to match the second cylinder, *the whole* of the first distillate must not be mixed with the Nessler-solution, else the colour produced would be too intense to allow of accurate judgment. In this case the volume of the first distillate is ascertained. 25 c.c., or even less, of the distillate are then diluted to 50 c.c. with ammonia-free water, before it is tested with the Nessler-solution in the manner already described. The total amount of ammonia in the first cylinder is then calculated.

The separate amounts of ammonia which have been found in the different portions of the distillate are then added

together, and from the total amount of ammonia thus found, the quantity per 100,000 is calculated.

Example.—The first cylinder required 0·6 c.c., and the second one 0·3 c.c. of the ammonium chloride solution; the total amount used is therefore $0·6+0·3=0·9$ c.c. Therefore half a litre, or 500 grams, of the water contains $0·9\times0·00005=0·000045$ gram of NH_3. Hence the water contains $0·000045\times200=0·009$ parts of NH_3 per 100,000.

For Interpretation of the Results refer to par. 563.

ESTIMATION OF ALBUMINOID AMMONIA.

535. Estimation of Albuminoid Ammonia.—When an organic substance containing nitrogen is heated with alkaline potassium permanganate solution, either a portion, or the whole of its nitrogen, is evolved as ammonia. The ammonia thus generated has been termed "albuminoid ammonia."

The fraction of the total nitrogen present in the same organic body, which is thus converted into ammonia, appears to be definite; but the fractions of the total nitrogen evolved as ammonia from different substances vary greatly. Hence this method would be of no value for estimating the amount of sewage contamination in a water, if the nitrogenous organic matter in sewage were not fairly uniform in its character. It is maintained that in ordinary water containing sewage, "the disintegrating animal refuse is pretty fairly measured by ten times the albuminoid ammonia which it yields."

An alkaline solution of potassium permanganate will be required for this estimation, in addition to the requisites for the process of estimating ammonia (528–533).

536. Preparation of Alkaline Potassium Permanganate Solution.—Pour about 44 c.c. of distilled water into a flask, add 10 grams of KOH and 0·5 gram of potassium permanganate. While the distillation for the estimation of NH_3 is proceeding, boil the above liquid vigorously. As soon as the liquid has been boiled down to about one-half its original volume, it is free from ammonia and is ready for use.

537. The Process of Estimating "Albuminoid Ammonia." —Add the alkaline potassium permanganate solution (536) to the liquid which is left in the flask after the estimation of the "free ammonia" (534, a), and pour in some water free from ammonia, if necessary, to furnish the necessary volume for distillation.

Boil the contents of the distillation flask over a naked flame (70) until at least four portions of 50 c.c. each have been collected in separate cylinders (531). Test each of these portions with Nessler-solution, starting with the last one. Reject any portions of the distillate which are practically free from ammonia.

If the quantity of ammonia in the distillate is believed to be small, the cylinders may be "Nesslerised" as is described in par. 534, b. If much NH_3 is present, either proceed as is there directed, or mix the several portions of the distillate together, measure the volume of the mixture, and test 50 c.c. of it with the Nessler-solution: then calculate the amount of ammonia present in the whole of the mixture.

Calculate from the whole amount of ammonia, which has been found in the distillate, the weight which is present in 100,000 of the water, as is shown in the Example (534).

For the Interpretation of the Results refer to par. 564.

Estimation of Organic Matter.

538. Estimation of the Oxygen Consumed by the Organic Matter, by the Forschammer or Oxygen Process. —This process enables a judgment to be formed as to the total amount of oxidisable matter present in water. In the absence of nitrites and of other inorganic reducing substances, the amount of oxygen required for the oxidation of the organic matter can be accurately determined by this process.

The process consists in mixing a known quantity of the water with acidified potassium permanganate solution, which oxidises the organic matter in the water. A measured volume of standard potassium permanganate solution is

employed, taking care that the permanganate is in excess. The excess is then estimated by adding potassium iodide solution ; and then titrating the iodine, which is liberated by the permanganate, with standard sodium thiosulphate solution and starch.

In order that the estimation may be as accurate as possible, equal volumes of the permanganate solution are added to equal volumes of the water and of pure distilled water (**788**). Both are allowed to stand for a fixed time ; and the excess of permanganate in each is then titrated as is described below. The difference between the two titrations indicates the amount of oxygen which has been consumed by the organic matter in the water.

The Following Solutions are required for this process.

(a). *Solution of Potassium Permanganate.*—Dissolve 0·395 .1975 gram of pure potassium permanganate in 1000 c.c. of water. 500 Each c.c. of this solution will contain 0·0001 gram of available oxygen.

(b). *Sodium Thiosulphate Solution.*—Dissolve 1 gram of pure recrystallised sodium thiosulphate in 1 litre of water.

(c). *Dilute Sulphuric Acid.*—Dilute 1 volume of pure strong sulphuric acid with 3 volumes of water.

(d). *Potassium Iodide Solution.*—Dissolve 1 part of pure recrystallised potassium iodide in 10 parts of water.

(e). *Starch Solution.*—Dissolve 1 part of starch in 100 parts of boiling water (**278**), and use the clear cold solution.

The Process of Estimating the Oxygen required by the Organic Matter.—Rinse out two 18-oz. conical flasks (A, B) first with strong sulphuric acid to destroy organic matter, and then with distilled water. Measure into one flask (A) 250 c.c. of pure distilled water (**788**), and into the other (B) 250 c.c. of the water under examination. Now measure into each flask 10 c.c. of the standard potassium permanganate solution (**a**), and 10 c.c. of the dilute sulphuric acid (**c**). Cover the two flasks with watch-glasses, and allow them to stand for three

hours. If the pink colour at any time disappears from the water in the flask, the process must be started afresh with 20 c.c. of the permanganate solution.

At the expiration of three hours, add to the flask (A) some of the potassium iodide solution (**d**). The pink colour of the permanganate will change to yellow, owing to the oxygen of the permanganate liberating its equivalent of iodine. Now add the thiosulphate solution (**b**) from a burette until the colour of the liquid in the flask fades to a pale straw tint. At this stage add 1 c.c. of fresh starch solution (**e**). A deep blue colour will appear: proceed to add more thiosulphate solution gradually until this colour entirely disappears.

Titrate the contents of flask (B) in a similar way.

The Process of Calculation.—Let x represent the number of c.c. of thiosulphate solution which have been used in the titration of the permanganate in the distilled water, and y the number of c.c. used in the titration of the permanganate in the water. Then $x-y$ is the number of c.c. of thiosulphate equivalent to the permanganate reduced by the organic matter in the water.

Further, if the amount of available oxygen in the 10 c.c. of permanganate originally added is represented by a, then the weight of oxygen required to oxidise the organic matter in 250 c.c. of the water will be $\frac{(x-y)a}{x}$. But $a = 0{\cdot}001$ gram of oxygen, and 250 c.c. of water were used, therefore the amount of oxygen consumed by 100,000 parts of the water $= \frac{(x-y)a \times 0{\cdot}001 \times 100{,}000}{x \times 250} = \frac{(x-y)0{\cdot}4}{x}$.

Example.—In a particular estimation 30 c.c. of the standard thiosulphate solution were required for the distilled water (A), and 25 c.c. for the water under examination (B). The amount of oxygen consumed per 100,000 parts was accordingly in this case $\frac{(30-25)0{\cdot}4}{30} = 0{\cdot}067$.

Factors for Calculation of the Organic Matter.—Attempts have been made to calculate the amount of organic matter in the water, from the quantity of oxygen which it consumes.

It has, however, been shown that no constant relation exists between the amount of oxygen consumed and the amount of organic matter present, except in the case of waters from similar sources; but by employing a proper factor, the approximate amount of organic carbon can be calculated from the oxygen consumed.

Thus in the case of river-waters, the weight of organic carbon is equal to that of the oxygen consumed multiplied by 2·38. In the case of deep-well waters the factor is 5·8; and factors have been determined for waters from other sources.

For the Interpretation of the Results refer to par. 565.

Estimation of Chloride.

539. Estimation of Chlorine as Chloride.—Chlorine is usually present in water in the form of sodium chloride, and its proportion is frequently reported in terms of that salt. The process of estimating chloride in water is identical with that described in paragraph **304**; standard solution of silver nitrate being added to the water, together with potassium chromate solution as an indicator. Accordingly the solutions required for the estimation are the following.

(a). *Standard Solution of Silver Nitrate.*—Dissolve 2·3944 grams of pure recrystallised silver nitrate in distilled water, and make the solution up to 1 litre. If 50 c.c. of water are used for titration, 1 c.c. of this solution represents 1 part of chlorine per 100,000 of the water.

(b). *Solution of Potassium Chromate.*—Dissolve 1 part of potassium chromate in 10 parts of water. The chromate solution must be freed from chloride by adding solution of silver nitrate until a permanent red precipitate is obtained; the liquid is then filtered.

The Process of Estimating Chloride.—Pour the silver nitrate solution (a) into a burette which is graduated into tenths of a c.c. Measure 50 c.c. of the water into a porcelain dish, and add three drops of the potassium chromate solu-

tion (b). Now add the silver nitrate solution, drop by drop, until a slight but permanent red colour is imparted to the liquid. This colour is due to the formation of silver chromate, after the whole of the chlorine has been precipitated as silver chloride.

It will be found convenient to prepare a similar dish containing 50 c.c. of water mixed with three drops of the potassium chromate solution, to which silver nitrate solution has been added, but not in excess. The slightest appearance of a reddish tint in the test-dish will then be easily seen, if the two dishes stand side by side for comparison.

The number of c.c. of the silver nitrate solution which have been used will give the weight of chlorine present in 100,000 parts of the water.

For the Interpretation of the Results refer to par. 566.

Estimation of Nitrite.

540. Estimation of Nitrite.—When an acid solution of meta-phenylene diamine is brought into contact with a weak solution of nitrous acid, a reddish-brown coloration is produced. A process for the estimation of nitrites is based upon this reaction. The following solutions are required for the estimation.

(a). *Solution of Meta-phenylene Diamine.* — Dissolve 5 grams of this substance in 1 litre of water, to which a little sulphuric acid has been previously added.

(b). *Dilute Sulphuric Acid.*—Add 1 volume of strong sulphuric acid to 2 volumes of distilled water.

(c). *Standard Solution of Sodium Nitrite.*—Dissolve 0·406 gram of pure silver nitrite in boiling distilled water. Add an excess of pure sodium chloride solution, so that the silver is completely precipitated as chloride. Now make up the liquid to 1 litre with distilled water. Allow the precipitate to subside; and make up each 100 c.c. of the clear liquid to 1 litre.

Since the solution undergoes oxidation when it is exposed to the air, and to daylight, it should be kept in small stoppered bottles, each of which is completely filled, and is stored in the dark.

Each c.c. of this solution corresponds to 0·00001 gram of N_2O_3.

The Process of Estimating Nitrite.—Measure 100 c.c. of the water into a perfectly colourless glass cylinder such as was used for the ammonia determination (531). The liquid should fill about three-fourths of the cylinder; and a file-mark should be made upon the side of the cylinder denoting the level when it contains 100 c.c.

Add 1 c.c. of the dilute sulphuric acid (b), then 1 c.c. of the meta-phenylene-diamine solution (a), and stir well with a glass rod. If a coloration is produced at once, a smaller quantity of the water must be taken, and this must be diluted up to 100 c.c. with pure distilled water. When the coloration only appears after the liquid has stood for one minute, the dilution will be sufficient.

An approximate measurement of the quantity of nitrous acid present is now made, by introducing different fractions of a c.c. of the standard sodium nitrite solution (c) into similar separate glass cylinders. Each is then made up to 100 c.c. with distilled water, and 1 c.c. of the acid and 1 c.c. of the meta-phenylene-diamine solution are added to each, as is described above.

It must be remembered that the colour develops only slowly, and that the comparison-cylinders will not have had so long a time for the development of colour as the original test-cylinder has had.

Hence, as soon as the approximate matching of colour has been effected, it will be necessary to make a fresh series of tests with the water and with the comparison-cylinders, all of which must be started at the same time. The colour of these liquids should be compared after they have been standing for twenty minutes.

For Interpretation of the Results refer to par. 567.

Estimation of Nitrogen in Nitrite and Nitrate.

541. Three methods are described.

According to the first (**542**) the nitrogen is converted into nitric oxide by the action of strong sulphuric acid and mercury, and the nitric oxide gas is measured.

In the second (**543**) the nitrogen is converted into ammonia by the action of the copper-zinc couple, and the ammonia is estimated by the Nessler colorimetric process.

In the third (**544**) the nitrate present is caused to form ammonium picrate, and this is estimated colorimetrically. This process estimates nitrate only, and not nitrite.

For the Interpretation of the Results of Analysis refer to par. **568**.

542. Estimation as Nitric Oxide, Crum's Method.—The most trustworthy method for estimating nitrite and nitrate is that devised by Crum. According to this method, the solution containing the nitrite and nitrate is shaken with strong sulphuric acid and mercury in a closed tube. The nitric oxide, which is thus evolved, is measured; and the weight of nitrogen which it contains is calculated. In the absence of other gas apparatus, the nitric oxide may be measured in a carefully calibrated Lunge nitrometer (**714**).

The Process of Estimation.—Add a small quantity of distilled water to the residue which was obtained in determining the total solids (**526**). Warm the dish on the steam-bath, and decant the liquid through a small filter into a little beaker. Repeat this operation two or three times. Then evaporate the contents of the beaker on the steam-bath down to about 2 c.c.

Fill the Lunge nitrometer (**714, 716**) completely with mercury; pour the liquid from the beaker into the cup (*f*) of the nitrometer, rinsing out the beaker with a very small quantity of water. Allow the solution to pass through the stopcock by gently turning the tap, taking care that no air enters. Now pour about double the volume of pure strong sulphuric (**543, c**) into the cup: and allow this to flow through the stopcock.

Both liquids are now mixed in the measuring-tube of the nitrometer; a considerable amount of heat is thus evolved. Bubbles of carbon dioxide gas and air may be evolved at this stage. As soon as they cease to rise, which will require a pause of about one minute, force out the gas which has collected, by gently opening the stopcock and raising the pressure-tube of the apparatus.

Then close the stopcock again, and violently agitate the measuring-tube so as to cause part of the mercury to mix up with the liquid. This is most readily effected by giving a rotatory as well as a vertical movement to the tube, as the mercury may in this way be broken up into small globules.

After the tube has been shaken for about two minutes, nitric oxide gas will be given off. The agitation must be continued until the evolution of gas ceases, which will usually be the case in about five minutes.

Now allow the liquid to cool down to the temperature of the air, and adjust the levels of the mercury columns as is described in paragraph **716**. Note down the atmospheric temperature and pressure, and proceed to calculate the weight of N in the NO.

The Calculation of Results.—The following example will explain the method of calculating the results.

Example.—In an estimation of nitrite and nitrate, 500 c.c. of the water yielded 3·3 c.c. of nitric oxide gas.

The atmospheric temperature was 20° C., and the atmospheric pressure 766 mm.

Therefore, the volume of the NO under normal conditions of temperature and pressure $= \frac{3{\cdot}3 \times 273 \times 766}{239 \times 760} = 3{\cdot}3 \times 0{\cdot}939$ (**778**).

And, since NO contains half its volume of N, and the weight of 1 c.c. of H = 0·0000896 gram,

the weight of N in the NO $= \frac{3{\cdot}3 \times 273 \times 766}{293 \times 760} \times 0{\cdot}0000896 \times 7 = 0{\cdot}00195$.

Since 500 c.c., of water were used, the weight of N per 100,000 $= 0{\cdot}0090 \times 200 = 0{\cdot}39$.

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543. Reduction of Nitrate and Nitrite to Ammonia by means of the Copper-Zinc Couple, and Estimation of the

Ammonia.—Zinc, upon which copper has been chemically deposited as a black film, constitutes a "copper-zinc couple." When this is immersed in the solution of a nitrate or nitrite, it converts the nitrogen completely into ammonia, which can then be estimated by means of Nessler solution.

The following substances should be prepared.

(a). *Pumice;* clean pumice is broken into pieces about the size of large shot. It is sifted free from powder, and is then heated to redness for some time. It is kept in a well-stoppered-bottle.

(b). *Hydrochloric Acid.*—Stong hydrochloric acid is tested for ammonia, by mixing half a c.c. of it with water free from ammonia, in a Nessler-cylinder (531), and adding 2 c.c. of Nessler-solution. If it is practically free from ammonia, 10 c.c. are diluted to 100 c.c. with ammonia-free water, and the liquid is preserved in a well-stoppered bottle.

The strong acid is freed from ammonia, if necessary, by distillation: collecting that part of the distillate apart, which comes over free from ammonia.

(c). *The Copper-Zinc Couple* is prepared by pouring a 3 per cent. solution of crystallised copper sulphate upon pieces of zinc. The zinc may be in the granulated condition; or it may be prepared by cutting strips of thin zinc sheet or foil, and folding them up. The deposition is allowed to go on until the zinc is covered with a firmly adherent black film of copper. This film must not be so copious as to be detached when the zinc is subsequently washed by gently shaking it several times with fresh quantities of water. About 5 grams of zinc should suffice for one estimation; and an immersion of 15 minutes in the copper solution usually produces a satisfactory copper film.

Process of Estimation.—The process must be conducted in a room which contains no ammonium salts, or other sources of ammonia; and before proceeding to make a determination of nitrate, a blank experiment should be made by the process described below, and any ammonia thus obtained must be subtracted from the ammonia found in an estimation.

The process may be carried out either with the water itself, or with the water extract of the solid residue (526). The latter is commonly used when the proportion of nitrate is small.

The ammonia which is produced from the nitrate as is described below may frequently be estimated directly without distillation (2); but distillation (1) is necessary when the water is coloured, or when the amount of nitrate is very small.

(1) *Estimation of the Ammonia by Distillation.* — The copper-zinc couple is prepared, as is directed above (**c**), in a 10-oz. stoppered fractionating-flask (**532**). After the metals have been washed in the flask, finally with ammonia-free water, the tubulure of the flask is connected with a U-tube filled with the pumice (**a**) moistened with the hydrochloric acid (**b**); one hundred c.c. of the water, or the equivalent extract of the water-residue (**526**), are now measured into the flask, which is at once stoppered, and is then allowed to stand for at least an hour.

If any doubt is felt as to the completion of the reduction, a small quantity of the liquid may be tested for nitrite by mixing it with dilute sulphuric acid and with meta-phenylene-diamine (**540**). As soon as no nitrite can be detected the reduction is complete.

Then add to the liquid about a gram of recently-ignited sodium carbonate crystals (**533**), and rinse in the pumice moistened with hydrochloric acid from the U-tube. Connect the tubulure of the flask with a Liebig-condenser, and proceed to distil over 50 c.c. Mix the distillate well, and measure 5 c.c. into a Nessler-cylinder (**531**). Dilute this with ammonia-free water, and add 2 c.c. of Nessler-solution. Proceed in this way to ascertain the whole amount of ammonia resulting from the reduction of the nitrate, using more than 5 c.c. of the distillate if necessary (**534, b**).

The amount of ammonia which has been found in the original water must be subtracted from the result thus obtained, unless it was removed before the reduction by the copper-zinc couple, and the weight of nitrogen which is contained in the ammonia is then calculated.

(2) *Direct Estimation of the Ammonia without Distillation.* —Two hundred c.c. of the original water, or the equivalent

extract of the water-residue, are mixed with a small quantity of oxalic acid solution, and are then allowed to stand in a well-stoppered bottle until the precipitate of calcium oxalate has completely subsided. The clear liquid is then divided into two equal portions (A, B) in two Nessler-cylinders.

The copper-zinc couple is allowed to act upon one portion (A) for an hour, as is described above (1), and as soon as the reduction to ammonia is complete the clear liquid is decanted into another cylinder. Two c.c. of Nessler-solution are then added to it. The comparison test is made by adding the requisite quantity of standard ammonium chloride solution to the other portion (B), followed by 2 c.c. of Nessler-solution (**534**, b).

In this way allowance is made for the ammonia originally present in the water, or in the oxalic acid: and for any turbidity caused in the liquid by the addition of Nessler-solution.

544. Conversion of Nitrate into Ammonium Picrate, and Estimation Colorimetrically. When phenyl-hydrogen sulphate solution is poured upon a nitrate, and sulphuric acid is added, picric acid is formed :—

$$(C_6H_5)HSO_4 + 3HNO_3 = C_6H_2(NO_2)_3OH + H_2SO_4 + 2H_2O.$$

The addition of ammonia in excess produces ammonium picrate, the yellow colour of which is easily seen even in very dilute solution. The intensity of the colour serves to estimate the picrate, and hence the nitrate from which it was produced.

This process estimates nitrate only, and not nitrite. If nitrite is present in the water, it must be specially estimated (**540**).

The following solutions are required.

(a). *Phenyl-Hydrogen Sulphate.*—55·5 c.c. of strong pure H_2SO_4 are added to 4·5 c.c. of water containing 9 grams of phenol. The liquid is shaken and is preserved in a tightly-stoppered bottle.

(b). *Standard Potassium Nitrate Solution.*—Some KNO_3 is

heated to a temperature just sufficient to fuse it, 0·722 gram of this is dissolved in water and diluted to a litre. Each c.c. of this solution contains 0·0001 gram of nitrogen.

The Process of Estimation.—A measured volume of water, usually 25 c.c., is evaporated to dryness in a small porcelain dish.

Five c.c. of the standard KNO_3 solution (b) are evaporated in another similar dish.

One c.c. of the phenyl sulphate (a) is added to each dish as soon as it is cold, and the contents of each dish are thoroughly mixed with small glass rods. One c.c. of distilled water is then added to each dish, followed by 3 drops of strong sulphuric acid. The liquids are well stirred, and the rods are rinsed into the dish with a little distilled water.

The dishes are heated on the water-bath for five minutes; each dish is then removed from the water-bath and its contents are diluted with 25 c.c. of distilled water and mixed with ammonium hydrate in excess. A deep yellow colour will appear in the standard solution, and also in the sample, if nitrate was originally present.

The liquid is now transferred from each dish to a separate graduated 250 c.c. closed cylinder, and is diluted to 100 c.c. with distilled water. 50 c.c. of the solution which shows the lesser intensity of colour are placed in a Nessler-cylinder (531). The more intensely coloured liquid is diluted with water and is well mixed by shaking. The dilution is continued until 50 c.c. of the liquid, when poured into a Nessler-cylinder, exactly matches in intensity the tint of the other liquid. The total volume in c.c. of the diluted liquid is then noted down, the volume of the other being 100 c.c.

The Formula for Calculating the number of parts of nitrogen present as nitrate in 100,000 of the water is

$$N = \frac{50 \times \text{Number of c.c. of the sample after dilution.}}{\text{No. of c.c. of the water used} \times \text{No. of c.c. of standard after dilution.}}$$

Example.—Thus in a particular case 25 c.c. of the water-sample were used. In the process of matching the colours the yellow liquid

from the water was made up to 100 c.c., while the yellow liquid from the standard nitrate solution was made up to 250 c.c. Hence N per $100{,}000 = \frac{50 \times 100}{25 \times 250} = 0{\cdot}8$.

Estimation of Hardness.

545. The "Hardness" of Water, or its soap-destroying power, depends upon the amount of calcium and magnesium salts which it contains, since these salts chemically act upon soap and precipitate it from solution. Other salts are occasionally present in water which act in a similar way upon soap; and sodium chloride precipitates soap from its solution in an unaltered state.

Hardness is of two kinds; "temporary hardness," which can be removed by boiling the water, and "permanent hardness," which cannot be removed in this way.

Two processes for the estimation of hardness are described.

Clark's Method (**546**) is the older process; it does not yield accurate results if a large quantity of magnesium salts is present.

Hehner's Method (**551**) gives on the whole better results, since the presence of magnesium salts does not materially affect its results.

For the Interpretation of the Results of Analysis refer to par. **569**.

546. Clark's Process for the Estimation of Hardness.—This method depends upon the fact that when solution of soap is mixed with solution of a calcium or magnesium salt, an insoluble calcium or magnesium soap is produced. Accordingly no lather will form when the water is shaken with soap-solution, until the soap-solution has been added in excess, and some soap therefore remains unaltered in the liquid.

The solution of soap in methylated spirit, which is used in this process, is first titrated by means of a standard

calcium chloride solution, and is then brought to the requisite strength. The water is then tested with this standard soap-solution. From the amount of soap-solution which is required to precipitate the hardening salts, the hardness of the water is obtained. The result is usually expressed in terms of calcium carbonate.

The following solutions are required for the estimation.

(a). *Standard Solution of Calcium Chloride.*— Weigh accurately 0·2 gram of pure Iceland spar. Dissolve this in dilute hydrochloric acid, taking care to keep the vessel covered, so as to prevent loss by spirting. Evaporate this solution to dryness on the water-bath. Add water, and again evaporate to dryness; and repeat this evaporation once at least, so as to remove all free hydrochloric acid. Now dissolve the residue of neutral calcium chloride in water, and make the solution up to 1 litre.

(b). *Preparation of Soap Solution.*—Potassium oleate soap is prepared by rubbing in a mortar 150 parts of lead plaster (Plumbi Emplast., *B.P.*) with 40 parts of dry potassium carbonate. When these have been thoroughly mixed, a little methylated spirit is added, and the substances are rubbed together until a cream is formed. The clear solution is stirred with more spirit, and is decanted after the sediment has subsided.

(c). *Titration and Dilution of Soap Solution.*—This strong soap-solution will now require dilution, until 14·25 c.c. of the solution just cause a *permanent* lather when they are shaken with 50 c.c. of the standard calcium chloride solution. Proceed as follows.

Mix the strong soap-solution with methylated spirit, which has been diluted with half its volume of water; and pour some of this solution into a burette. Measure 50 c.c. of the calcium chloride solution (a) into a stoppered bottle of 250 c.c. capacity, allowing the liquid to flow out of the pipette, without blowing any carbon dioxide from the lungs into the bottle.

Now allow 1 c.c. of the soap-solution to flow from the burette into the bottle, close the bottle and shake it vigorously for a short time. If no permanent lather is produced, add another c.c. and shake again.

Continue to add the soap-solution and to shake well, until a lather is formed and remains for a short time when the bottle is laid upon its side on the bench. The process is finished when the lather remains as an unbroken layer for two minutes. If magnesium salts are present, the lather should be produced *a second time* by shaking, and must last again for two minutes.

Towards the end of this operation, the amount of soap-solution which is added should be lessened; and towards the finish it should not exceed one-fifth of a c.c. Experience renders it possible to detect the approach of the end of the reaction by the sound and sensation produced during shaking, since the sound and shock become much more gentle when a lather begins to form.

The soap-solution can now be diluted from calculation (237) until exactly 14·25 c.c. of it are required to produce the lather with 50 c.c. of calcium chloride solution.

The strength of the soap-solution should be checked after it has stood for about 24 hours, since a sediment usually forms which reduces its value. It is on this account preferable to defer the final dilution and titration, until no further sediment is deposited.

(c). **Another Method of Preparing the Soap-Solution** is to dissolve 80 grams of chemically pure oleic acid in alcohol. A few drops of phenol-phthalein are added to this solution, and a strong solution of potassium hydrate in alcohol is gradually added until the oleic acid is exactly neutralised, and saponification is therefore complete. This is indicated by the liquid retaining a faint purple coloration. The solution is then titrated with the standard calcium chloride solution (a), and is diluted to standard strength (c).

547. *Estimation of the Total Hardness.*—Measure 50 c.c. of the water into a stoppered bottle of 250 c.c. capacity. Shake the water well, and then remove any carbon dioxide which is evolved, by sucking out the air from the upper

part of the bottle by means of the pipette; repeat these processes (see *Note*). Then proceed to titrate the water with the standard soap-solution in the manner described under **546**, c.

If more than 16 c.c. of soap-solution are required by the water, dilute a suitable quantity of the water to 50 c.c. with boiled distilled water (see *Note*), and titrate again.

The number of degrees of hardness in the water, expressed as parts of calcium carbonate per 100,000, may now be obtained from the number of c.c. of soap-solution used, by reference to the following Hardness Table (**548**).

If much magnesium salt is present, it will be found difficult to ascertain the end of the process. This is partly due to the formation of a permanent scum upon the water; but also to the fact that the soap-solution acts much more slowly upon magnesium salts than it does upon calcium salts. When magnesium salts are present, it is best to dilute the water until not more than 7 c.c. of the soap-solution are required for the titration.

Note.—Various precautions are mentioned in the above description of the process for determining the hardness, with the object of preventing the introduction of carbonic acid. Carbonic acid acts chemically upon soap in such a way as to prevent it from giving a lather when its solution is shaken. Hence, before adding any soap-solution to a measured sample of water, the sample should be repeatedly shaken vigorously in the bottle, and the CO_2 liberated should be sucked out by a tube after each shaking. For the same reason all distilled water used for dilution, or for making solutions, should have been recently boiled and quickly cooled.

549. *Estimation of the Permanent Hardness.*—The method consists in boiling the water until all the hardening salts, which are precipitable by boiling, are deposited. The liquid is then made up to its original volume with distilled water, and is filtered if necessary. The hardness is determined in the clear filtrate.

Measure about 250 c.c. of the water into a flask and weigh the flask with the water. Boil the water gently for half an hour, adding boiled distilled water from time to time, to

HARDNESS TABLE.

548. Parts of $CaCO_3$ per 100,000.

c.c. of Soap-solution.	Parts of $CaCO_3$.	c.c. of Soap-solution.	Parts of $CaCO_3$.	c.c. of Soap-solution.	Parts of $CaCO_3$.	c.c. of Soap-solution.	Parts of $CaCO_3$.	c.c. of Soap-solution.	Parts of $CaCO_3$.	c.c. of Soap-solution.	Parts of $CaCO_3$.
0·7	·00	3·3	3·64	5·9	7·29	8·5	11·05	11·1	15·00	13·7	19·13
8	·16	·4	·77	6·0	·43	·6	·20	·2	·16	·8	·29
·9	·32	·5	·90	·1	·57	·7	·35	·3	·32	·9	·44
1·0	·48	·6	4·03	·2	·71	·8	·50	·4	·48	14·0	·60
·1	·63	·7	·16	·3	·86	·9	·65	·5	·63	·1	·76
·2	·79	·8	·29	·4	8·00	9·0	·80	·6	·79	·2	·92
·3	·95	·9	·43	·5	·14	·1	·95	·7	·95	·3	20·08
·4	1·11	4·0	·57	·6	·29	·2	12·11	·8	16·11	·4	·24
·5	·27	·1	·71	·7	·43	·3	·26	·9	·27	·5	·40
·6	·43	·2	·86	·8	·57	·4	·41	12·0	·43	·6	·56
·7	·56	·3	5·00	·9	·71	·5	·56	·1	·59	·7	·71
·8	·69	·4	·14	7·0	·86	·6	·71	·2	·75	·8	·87
·9	·82	·5	·29	·1	9·00	·7	·86	·3	·90	·9	21·03
2·0	·95	·6	·43	·2	·14	8	13·01	·4	17·06	15·0	·19
·1	2·08	·7	·57	·3	·29	·9	·16	·5	·22	·1	·35
·2	·21	·8	·71	·4	·45	10·0	·31	·6	·38	·2	·51
·3	·34	·9	·86	·5	·57	·1	·46	·7	·54	·3	·68
·4	·47	5·0	6·00	·6	·71	·2	·61	·8	·70	·4	·85
·5	·60	·1	·14	·7	·86	·3	·76	·9	·86	·5	22·02
·6	·73	·2	·29	·8	10·00	·4	·91	13·0	18·02	·6	·18
·7	·86	·3	·43	·9	·15	·5	14·06	·1	·17	·7	·35
·8	·99	·4	·57	8·0	·30	·6	·21	·2	·33	·8	·52
·9	3·12	·5	·71	·1	·45	·7	·37	·3	·49	·9	·69
3·0	·25	·6	·86	·2	·60	·8	·52	·4	·65	16·0	·86
·1	·38	·7	7·00	·3	·75	·9	·68	·5	·81		
·2	·51	·8	·14	·4	·90	11·0	·84	·6	·97		

replace the water which evaporates. Now cool the water quickly, and make up the flask and water to their original weight (*Note*) with cold recently boiled distilled water (**547**, *Note*). Mix well and pour the water through a dry filter. Titrate a suitable volume of the filtrate with soap-solution as was described in par. **547**.

The degrees of Permanent Hardness are then obtained by reference to the Hardness Table (**548**).

Note.—It is evident that another method is to take an exactly measured volume of the water, and to dilute the water to the same volume after it has been boiled and filtered. This procedure is less rapid in practice.

550. *Temporary Hardness.*—The difference between the Total Hardness and the Permanent Hardness gives the Temporary Hardness of the water.

551. Hehner's Method for the Estimation of Hardness.—In this process, the calcium and magnesium carbonates, which cause the temporary hardness, are first determined by titration with standard acid. Both the carbonates and sulphates of calcium and magnesium are then precipitated by adding a known volume of standard sodium carbonate solution in excess and boiling for half an hour (*Note* 1). The unchanged sodium carbonate is then estimated by means of standard acid (*Note* 2). The amount of sodium carbonate which is decomposed by the above sulphates is thus found, and from this the permanent hardness can be calculated.

Note 1.—If magnesium salts are present, the liquid should be evaporated to dryness with the sodium carbonate, the excess of which is then extracted from the residue by water and estimated by titration with the standard acid.

Note 2.—If this process is used for water which contains sodium carbonate, a correction must be applied (p. 334).

Methyl-orange is used as an indicator in these titrations, because it is not affected by carbonic acid.

The following solutions are required.

(a). *Deci-normal Sulphuric Acid.* — Dilute 100 c.c. of normal sulphuric acid (**236**) to 1 litre.

(b). *Deci-normal Sodium Carbonate Solution.*—Dissolve 5·306 grams of pure dry sodium carbonate (**233**) in water, and make this solution up to 1 litre. The solution may also be prepared by diluting 100 c.c. of normal sodium carbonate solution (**233**) to 1 litre.

Estimation of the Temporary Hardness.—Add to 500 c.c. of the water, or less if it is very hard, a few drops of methyl-orange (**227**). Then add the deci-normal sulphuric acid (a) from a burette, until the colour of the solution changes to the red tint. From the number of c.c. used, the corresponding amount of $CaCO_3$ can be calculated; and this is converted into parts per 100,000.

Estimation of the Permanent Hardness.—To 250 c.c. of the water add 50 c.c. of the deci-normal sodium carbonate solution (b), and boil for about half an hour. If magnesium salts are present, refer to *Note* 1 (p. 333). Filter, and wash the precipitate with boiled distilled water, making the cold filtrate up to 250 c.c.

Titrate 50 c.c. of the filtrate with the deci-normal acid (a), using methyl-orange as an indicator.

From the number of c.c. of acid used, the permanent hardness can be calculated in terms of $CaCO_3$; this is then converted into parts per 100,000.

The Total Hardness may be obtained by adding together the temporary and the permanent hardness.

Estimation of Sodium Carbonate.—When the water contains sodium carbonate no permanent hardness will be present. The amount of sodium carbonate can easily be estimated by means of the standard acid (a), since the sodium carbonate will remain in solution after the water has

been boiled, and can therefore be titrated in the filtrate after the carbonates of magnesium and calcium have been precipitated by boiling the water (549).

Example.—In an estimation of temporary hardness in a water, 500 c.c. of the water required 8·4 c.c. of deci-normal sulphuric acid. Since 1 c.c. of this acid corresponds to 0·005 gram of $CaCO_3$, therefore the weight of $CaCO_3$, which would neutralise the acid, is $8{\cdot}4 \times 0{\cdot}005 = 0{\cdot}042$ gram. Hence the parts of calcium carbonate per $100{,}000 = 200 \times 0{\cdot}042 = 8{\cdot}4$.

In estimating the permanent hardness 250 c.c. of the water were boiled with 50 c.c. of deci-normal sodium carbonate solution, and after filtration the filtrate was made up to 250 c.c. Fifty c.c. of this liquid required 3·6 c.c. of deci-normal sulphuric acid for neutralisation.

Hence the permanent hardness in the 50 c.c. used corresponds to $10 - 3{\cdot}6 = 6{\cdot}4$ c.c. of deci-normal sodium carbonate solution, since 10 c.c. of Na_2CO_3 solution were present for every 50 c.c of the solution. Therefore the number of c.c. of Na_2CO_3 solution corresponding to the permanent hardness in the 250 c.c. of the water used is $= 6{\cdot}4 \times 5 = 32$. And since 1 c.c. of the sodium carbonate solution corresponds to 0·005 gram of $CaCO_3$, the permanent hardness in 100,000 parts $= 32 \times 0{\cdot}005 \times 400 = 64$.

Hence the total hardness $= 64 + 8{\cdot}4 = 72{\cdot}4$.

ESTIMATION OF OTHER CONSTITUENTS OF THE WATER.

For most purposes the estimations described above are sufficient. But other processes are appended which will serve for the detection and estimation of poisonous metals, and for certain estimations required for technical purposes.

Detection and Estimation of Poisonous Metals.

552. Copper and lead are the most commonly occurring poisonous metals in water: arsenic, barium, and zinc may be tested for in exceptional cases.

Copper and lead are detected by evaporating a measured quantity of the water to a small bulk, rendering it just acid with a few drops of hydrochloric acid, and then passing a current of hydrogen sulphide gas through the liquid for some time. A brown coloration will show the presence of one or both of these metals.

553. Estimation of Copper.—Prepare a standard copper sulphate solution containing 0·3929 gram of crystallised copper sulphate per litre. Each c.c. of this solution corresponds to 0·0001 gram of copper.

Evaporate 500 c.c. of the water to 50 c.c. Add a little acetic acid, and a few drops of very dilute potassium ferrocyanide solution. If copper is present, a reddish-brown tint will appear.

This tint is matched in 50 c.c. of distilled water acidified with acetic acid, and mixed with the same quantity of potassium ferrocyanide solution, by adding a suitable measured volume of the standard copper solution.

The weight of copper present in 100,000 parts of the water $= n \times 0{\cdot}0001 \times 200 = n \times 0{\cdot}02$, where n represents the number of c.c. of the standard copper solution which were required by 500 c.c. of the water.

554. Estimation of Lead.—If copper is absent lead may be estimated by the following method.

Prepare a standard lead acetate solution, containing 0·1831 gram of normal lead acetate per litre. Each c.c. of this solution corresponds to 0·0001 gram of lead.

Evaporate 500 c.c. of the water down to 50 c.c., add a few drops of acetic acid, and pour off the liquid into a clear glass cylinder (**531**). Then add 2 c.c. of hydrogen sulphide solution: a brownish or black tint will be produced.

Now pour 50 c.c. of distilled water into a second cylinder; add a measured quantity of the standard lead acetate solution, and then add 2 c.c. of hydrogen sulphide solution. If the colour in this comparison-cylinder is not as deep as that in the test-cylinder, add the lead solution gradually, with

constant stirring, until the coloration is of equal intensity in both cylinders.

The weight of lead present is then calculated as in the estimation of copper (553).

555. **Action of Water on Lead.**—Many natural waters act upon lead, and become poisonous by this action. Since water which is used for drinking purposes often comes into contact with lead or lead-alloy, it is advisable to ascertain whether such water has any action upon lead.

As a rule, rain-water and very soft waters act upon lead, while hard waters do not unless they contain much carbonic acid. This is due to the fact that the hardening constituents of hard waters rapidly form an insoluble coating upon the surface of the lead, which prevents the further action of the water.

In order to test the behaviour of a sample of water towards lead, prepare two strips of sheet-lead. One of these is scraped so as to present a bright surface, while the other is left tarnished by previous exposure to air and water. Immerse the lead strips in separate beakers of the water, and allow them to stand undisturbed for 24 hours. Then note the appearance of the lead and of the water.

If the surface of the lead has remained unchanged in appearance, and the water is perfectly clear and bright even after it has been shaken, the water has probably not acted upon the lead. As a further precaution, remove the strips, and test the water for lead with hydrogen sulphide, as has been described above (554).

Estimation of Mineral Constituents.

556. **Estimation of Iron.**—Evaporate 500 c.c. of the water to dryness, after adding a few drops of nitric acid free from iron. Dissolve the residue in 50 c.c. of water, pour the solution into a glass cylinder (531), and add 1 c.c. of very dilute potassium ferrocyanide solution.

If a blue colour develops on standing, compare with it under similar conditions 50 c.c. of distilled water, to which a definite quantity of a standard solution of ferric salt containing 1 decigram of Fe per litre has been added. This solution may be prepared as is described in paragraphs **255**, **257**, but it must be boiled with a slight excess of nitric acid before it is diluted.

If iron is present in large quantity, it may be estimated by paragraphs **557**, **558**.

557. Estimation of Silica.—Acidify a litre of the water with hydrochloric acid, and evaporate it to dryness. Dry the residue perfectly on the steam-bath; then moisten it with hydrochloric acid, add water, and heat. Filter off any insoluble residue of silica, and wash, ignite, and weigh it. Preserve the filtrate.

558. Estimation of Iron and Calcium.—If iron is present in any quantity (**556**), add a few drops of strong nitric acid free from iron to the filtrate from the silica (**557**), and boil. Then add a little ammonium chloride solution, and a slight excess of ammonium hydrate. Filter off the ferric hydrate; ignite, and weigh it as Fe_2O_3 (**92**).

To the filtrate add excess of ammonium oxalate solution; allow the liquid to stand; filter off the calcium oxalate, ignite it, and weigh as oxide (**109**, **111**).

559. Estimation of Magnesium.—Evaporate the filtrate from the calcium oxalate to dryness. Expel the ammonium salts by heat. Dissolve the residue in hydrochloric acid, add water, and filter if necessary. Then add a moderate excess of ammonium hydrate, and then sodium phosphate solution. Filter, wash and ignite the precipitate, weighing it as pyrophosphate (**130**).

560. Estimation of Sulphate.—Acidify 500 c.c. of the water with hydrochloric acid, and evaporate to about 50 c.c. Add barium chloride solution in excess. Filter, and weigh the precipitate of barium sulphate (**96**).

561. Estimation of the Alkali-Metals.—Concentrate a litre of water by evaporation to about 100 c.c. Precipitate the sulphate completely with barium chloride solution. Filter, and boil the filtrate with milk of lime to precipitate the iron and magnesium. Filter; add to the filtrate excess of ammonium hydrate, then ammonium carbonate solution and a few drops of ammonium oxalate solution, to precipitate the barium and calcium in solution. Filter; evaporate the filtrate to dryness, and ignite the residue to drive off ammonium salts.

Extract the residue with water, filter if necessary, and test with one drop of ammonium oxalate solution to ascertain that all the calcium is precipitated. Filter again, if necessary; acidify with hydrochloric acid; evaporate to dryness in a weighed dish; ignite gently, and weigh the alkaline chlorides (358). The amounts of potassium chloride and of sodium chloride may then be estimated, if necessary, directly indirectly (359).

GENERAL REMARKS ON THE RESULTS OF THE CHEMICAL EXAMINATION OF WATER.

Note.—The results of the above estimations are expressed in parts per 100,000: they can be converted into grains per gallon by being multiplied by 0·7.

562. Total Solid Residue (526).—Those waters, which leave a large residue on evaporation, are unsuited for manufacturing purposes; since they involve waste of soap, and produce scale in steam-boilers. Such waters are not necessarily undesirable for drinking purposes.

The amount of residue usually depends upon the nature of the soil through which the water has percolated. River-water usually contains from 10 to 30 parts of dissolved matter per 100,000. Shallow well-water may contain from

30 to 200 parts or even more, the variation in this class of waters being very great. Deep well-waters may contain from 20 to 70 parts, but the proportion varies considerably.

The weight of total solids should be approximately equal to the sum of the weights of the constituents estimated separately.

563. The Ammonium Salts (527) present in water are almost invariably of animal origin. Their presence usually points to *recent* sewage contamination, since ammonia is one of the first products of change of nitrogenous animal refuse. Ammonia, when it is dissolved in water which contains calcium or magnesium carbonates, is readily oxidised to nitrite and nitrate; hence arises the necessity for estimating it as soon as possible after the water has been collected.

The amount of ammonia which is present as ammonium salts in water varies greatly.

Upland Surface water usually contains about 0·002 per 100,000, but the amount may exceed 0·008. If the land through which the water passes is manured, the amount of ammonia may rise to 0·03 or even higher.

Shallow Well waters contain amounts of ammonia varying from nothing up to 2·5.

Deep Well water may contain as much as 0·1, but 0·01 may be taken as an average quantity. The presence of a high proportion of ammonia in a deep well-water casts suspicion on the water if the albuminoid ammonia rises above a mere trace, or if any appreciable amount of oxygen is required in the permanganate test.

Spring water contains but little ammonia, seldom more than 0·01; the average amount is about 0·001.

Sewage may contain as much as 10 parts.

As a rule, it may be stated that water must be considered suspicious, if it contains as much as 0·01 of ammonia per 100,000.

564. Albuminoid Ammonia, as has been already explained (535), gives an indication of the amount of organic nitrogenous matter present in the water. It should not exceed 0·008 parts per 100,000.

565. Oxygen Consumed by the Organic Matter (538).—The relative freedom from organic impurity of water from different sources, may be judged from the results of the permanganate process by the following standards. The weight of oxygen required for 100,000 parts of the water is stated in the Table.

	Upland Surface-water.	Water from other sources.
Water of:—		
Great purity, .	Not exceeding 0·1.	Not exceeding 0·05.
Medium purity, .	From 0·1 to 0·3.	From 0·05 to 0·15.
Doubtful purity, .	From 0·3 to 0·4.	From 0·15 to 0·2.
Impure, . .	Exceeding 0·4.	Exceeding 0·2.

566. Chloride (539) is usually present in water as sodium chloride, occasionally as calcium or other chloride. The chloride present in water may occasionally be derived from soil containing salt; or from sea-water, which is either mixed with the water, or has been introduced as spray, which may travel inland to great distances. If no such source of the chloride can be traced, it may be considered to be derived from urine if it exceeds 2 parts per 100,000.

Rain water itself usually contains sodium chloride, which is derived from the air.

Spring and River waters, if they are unpolluted with animal refuse, usually contain less than 1 part per 100,000.

Shallow Well water may contain almost any amount of chloride, the proportion depending on the extent to which sewage has percolated into the well.

567. Nitrite (540), if it is present in any appreciable quantity, should be regarded as an indication of comparatively recent sewage contamination. Nitrite is readily oxidised to nitrate. Both nitrate and nitrite are themselves innocuous, but they show that objectionable organic matter may have been introduced into the water.

Nitrite in *Deep Well water* has been probably produced by the deoxidation of nitrate. The presence of nitrite in deep well-water is therefore not looked upon with as much suspicion as when it is found in *Shallow Well* or in *Upland Surface* water, unless albuminoid ammonia or organic matter is also present in appreciable quantity.

568. Nitrogen as Nitrite and Nitrate (541).—The estimation in water of the nitrogen present as nitrite and nitrate is of importance for the following reason.

When nitrogenous organic matter is fully oxidised, its nitrogen remains chiefly in the form of nitrate; but nitrite is also occasionally present if the oxidation is incomplete. Thus, the presence of a large amount of nitrogen as nitrite and nitrate points to past sewage contamination. This implies that, if the filtration and aeration which have caused the oxidation of the organic matter should fail, there will be the risk of recent unoxidised sewage matter being present in the water. Such a risk is, however, practically absent in the case of water drawn from well-constructed deep wells.

Upland Surface water, if uncontaminated, should not contain more than 0·03 of nitrogen as nitrate and nitrite per 100,000, although in cultivated districts the amount may reach 1 part per 100,000.

In Shallow Well waters the amount varies greatly.

In Deep Well water the amount may rise to 5 parts, but the average is only 0·5.

569. The Degree of Hardness of water (545) is chiefly of importance, when the water is used for cleansing or for manufacturing purposes, or for steam-boilers.

If the water is required for drinking purposes, the hardness may vary from 2 to 50 parts per 100,000. This variation in the hardness seems to have no effect upon the health of the consumers. But for technical uses a very hard water is objectionable. The character of the hardness will vary with the nature of the soil through or over which the water flows.

Water may be Softened by the removal of its temporary hardness by treatment with Clark's process. This consists in adding sufficient milk of lime to neutralise the carbonic acid in the water. The calcium hydrate thus added is precipitated as carbonate, together with the dissolved carbonates. A certain slight degree of hardness, due to calcium carbonate, always remains, since calcium carbonate is soluble to a small extent in water free from carbonic acid.

It has been found that the addition to 700 gallons of the water of 1 oz. of quicklime for each degree of temporary hardness per 100,000 yields a good result.

For technical purposes, both the temporary and permanent hardness may be removed, by the addition of a mixture of sodium hydrate and sodium carbonate. The removal of calcium salts is more complete if solution of an alkaline oxalate is added in slight excess.

SECTION III.

ANALYSIS OF FOOD, TANNING MATERIAL, AND SOAP.

580. Introductory Remarks.—In this Section certain processes for the chemical examination of Food are described. Those which are most frequently in use, and are more or less typical, have been selected. A few analyses of Technical Products are appended.

For fuller information on analyses of this nature, the student is referred to the following books:—

Hassall's Food Analysis;
Allen's Commercial Organic Analysis;
Hehner's and Angel's Butter Analysis;
Wanklyn's Milk Analysis;
Procter's Text-book of Tanning;
The Analyst;
The Analytical Section of the Journal of the Society of Chemical Industry.

Analysis of Milk.

581. The following estimations are usually made in milk:—total solids, ash, and fat. From the results of these estimations the amounts of water and of "solids not fat" are deduced. The casein and milk-sugar, which are included in the latter term, are rarely estimated separately.

582. Estimation of Total Solids.—Mix the sample of milk well, and measure 5 c.c. into a small weighed platinum dish. Then weigh the dish with the milk, in order to ascertain the weight of the 5 c.c. of milk.

Evaporate the milk to dryness upon the steam-bath. Transfer the dish with the residue to the steam-oven, and continue to heat it until its weight is constant, or practically so. About five hours is usually necessary to complete this process of drying.

583. Estimation of Ash.—Ignite the residue in the platinum dish (582) over a Bunsen or Argand flame, at a temperature which never approaches visible redness. If the temperature is too high, part of the chlorides will be volatilised. Continue the ignition until all volatile matter is driven off. Allow the dish to cool, and weigh it.

584. Estimation of Fat.—Several methods for estimating the fat are in vogue, three of which are described below (585–590). A fourth method (591) is added, which involves no special process of estimation.

585. First Method for Estimating Fat.—This method depends upon extracting the fat from the dry residue of the milk by ether, and weighing the fat thus obtained.

Weigh 10 c.c. of the milk in a stoppered weighing-bottle, and pour it upon about 20 grams of silver-sand or of anhydrous plaster of Paris, contained in a porcelain evaporating dish about 3 inches in diameter. The sand should have been previously freed from soluble matter, by treating it with hydrochloric acid and then washing it with water.

Place the dish on the water-bath, and heat it until the sand is dry, stirring continually, in order to prevent the formation of lumps.

The fat may be most conveniently removed from this residue by extraction with ether in the Soxhlet apparatus (589). The following method is more tedious.

Transfer the residue from the dish to a wide-mouthed

8-oz. round flask; detaching the last portions, if necessary, by using a little ether and a glass rod.

Heat the residue in the flask with about 50 c.c. of anhydrous ether. For this operation the flask should be connected with a reflux Liebig-condenser, so that the ether, as it is boiled off, may be condensed and caused to flow back again into the flask.

After the ether has been boiled for about half an hour, pour off the ethereal extract of the fat through a dry filter into a weighed flask. Repeat these operations with another 50 c.c. of ether, and pour it off through the filter into the same flask as before.

Finally wash the sand, which still contains a little fat, with more ether, until no residue of fat is left when a few drops of the ether are evaporated to dryness on a watch-glass. These washings are added to the ether-extract which is already in the flask.

Distil off the ether from the fat-extract, as far as possible, condensing the ether vapour by means of a Liebig-condenser. Remove the flask to the water-bath, and heat it for some time; finally heat it in the steam-oven, until its weight is constant.

It will probably be found convenient to distil off the ether from the first ethereal solution of fat, as soon as it is filtered into the tared flask. The subsequent extracts and washings are then poured into the same flask, and subjected to distillation later on.

586. The Werner-Schmid Method for Estimating Fat.—In this method the milk is treated with hydrochloric acid and heated. The acid attacks the casein which incloses the fat-globules, and thus renders the fat easily soluble when ether is added and the liquid is vigorously shaken. The volume of the ethereal solution is noted. An aliquot measured part of it is removed into a small weighed dish, and the ether is evaporated. From the weight of fat thus obtained, the whole amount of fat dissolved by the ether can be calculated.

Shake the milk well, and transfer 10 c.c. of it to a Schmid-tube (fig. 77), which is graduated into 50 c.c. Add 10 c.c. of strong hydrochloric acid. Close the bottle with a cork, and heat it on the water-bath for about ten minutes with occasional shaking. The liquid will become dark brown in colour, owing to the chemical action of the acid upon the casein.

FIG. 77.

Now cool the liquid rapidly, by holding the tube in a stream of cold water. When it is perfectly cold, fill the tube to the 50 c.c. graduation with ether, which has been freed from alcohol by washing it repeatedly with water. Insert the cork, and shake the liquid vigorously for one minute.

Then allow the ether to rise to the surface. When the ether has separated, a small layer of undissolved matter will be seen between the ethereal and acid portions of the liquid. The volume of the ether is read off from the middle of this layer of undissolved matter to its upper surface.

Measure off rapidly two 10 c.c. portions of the ether solution into separate tared porcelain dishes. Evaporate these to dryness on the water-bath. Then remove the dishes to the steam-oven, and heat them until their weights are constant.

From the mean total weight of fat which is obtained from these two estimations, the percentage of fat in the milk can be calculated.

Example.—In an actual estimation, 10 c.c. of milk were used. After agitation with ether, the ethereal solution measured 28 c.c. The evaporation of 10 c.c. of this solution yielded 0·124 gram of fat.

Hence 10 c.c. of the milk contained $\frac{0{\cdot}124 \times 28}{10} = 0{\cdot}347$ gram of fat.

Therefore 100 c.c. of the milk contain 3·47 grams of fat.

587. Adams' Method for Estimating Fat.—This method consists in allowing a known weight of milk to be absorbed by a strip of filter-paper. The water is then evaporated

from the paper by heat; and the fat is subsequently removed by means of hot ether in an extraction apparatus. The resulting ether solution is distilled, and after the ether has been driven off, the residual fat is weighed.

This process possesses the advantage of rapidity of execution, since the fatty matter presents a very large surface to the solvent action of the ether. The removal of the fat is also very complete, when it is effected in an ordinary extraction apparatus. The filter-paper and extraction apparatus, which are required for this process, are described below.

588. *Filter-paper Strips.*—These strips are $22\frac{1}{2}$ inches long, and about $2\frac{1}{2}$ inches wide. The width will depend upon the dimensions of the reservoir of the Soxhlet extraction apparatus (fig. 78, *b*). The strips should be of such a width, that when coiled up and placed in the reservoir of the Soxhlet-apparatus, they reach nearly to the upper bend of the syphon-tube (*b*).

Paper free from fat and from other matter soluble in ether may be purchased for use in this process.

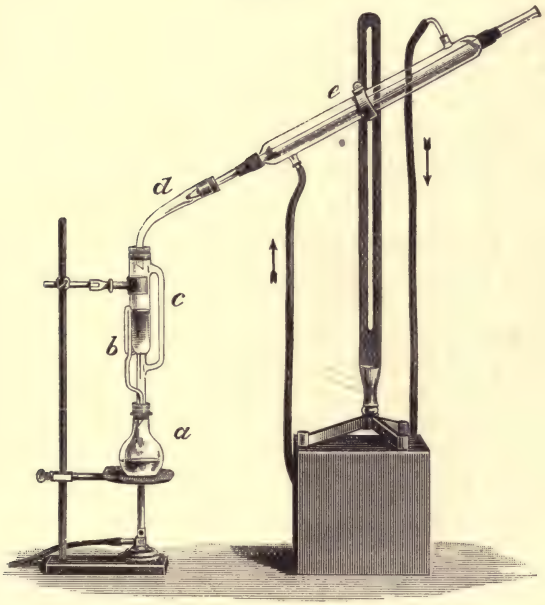
If ordinary Filter-paper or Blotting-paper is used, the matter soluble in ether may either be estimated and allowed for, or, better still, the paper is freed completely from fatty matter, soap and resin by the treatment described under par. 589 before it is used in the process. If the fatty matter is to be allowed for, proceed to ascertain the loss of weight which five similar strips of the paper suffer, when they are treated with ether in a Soxhlet-apparatus, as is described below (589). From this result the average weight of the soluble matter in one strip may be calculated; and this weight, which usually amounts to from 10 to 12 milligrams, is subsequently subtracted from the weight of the milk extract.

589. *The Soxhlet Extraction Apparatus.*—A suitable extraction apparatus is shown ready for use in fig. 78. The flask (*a*) contains the solvent liquid. The neck of this flask is connected with the Soxhlet-extractor (*b*, *c*), by means of an ordinary cork, the lower end of the extractor being pushed through a perforation in the cork. Into the upper end of the extractor another cork is fitted, through a per-

foration in which passes the end of the adapter (*d*). The adapter is a conical piece of glass tube, bent as is shown in the figure; it enables the Liebig-condenser (*e*) to be attached at a convenient angle. In fitting the apparatus ordinary corks must be used, which have been previously extracted with ether.

The requisite quantity of ether or other solvent is poured into the flask (*a*), and the paper or other substance to be

FIG. 78.



operated upon is placed in the broad central tube of the extractor (*b*, *c*). The substance should not reach higher than the shaded portion in the figure: it is usually placed in a bag made of filter-paper, so that no solid matter can find its way into the reservoir, and thence through the side-tube (*b*) into the flask (*a*).

When the liquid in the flask (*a*) is boiled, its vapour passes

up through the lower central tube, and thence through the side-tube (*c*), since there is no communication between the reservoir and the lower central tube. The vapour then passes into the condenser, and the condensed hot liquid drops back from the adapter (*d*) upon the substance in the reservoir.

As soon as the liquid in the reservoir reaches the level of the upper bend of the narrow syphon-tube (*b*), which communicates with the bottom of the reservoir, it fills that tube and syphons over, and thus finds its way back again to the flask (*a*). This process will repeat itself as often as the liquid, collecting in the reservoir, reaches the necessary level. In this way the substance is constantly brought into contact with the pure hot solvent; and the matter thus extracted is carried by the solvent into the flask (*a*), where it will remain.

The Liebig-condenser is attached to prevent loss of the solvent by evaporation.

590. *The Process of Extracting the Fat.*—Place one of the strips of filter-paper (**588**) upon a flat surface; then lay along the paper a piece of string of such a length, that 6 inches of it project beyond one end of the paper. Now roll the paper up into a coil, keeping the string in the interior. The string will prevent the successive coils of the paper from touching one another; the whole surface of the paper will therefore be exposed to the action of the solvent during the extraction. Tie the free end of the string round the paper-coil, and make a loop in it, by means of which the coil can be suspended.

If the paper-coil and string are not already free from fat, soap, and resin, they must be treated as follows. Place the coil and string in the extractor (fig. 78). Half fill the flask (*a*) with alcohol, which is rendered distinctly acid with glacial acetic acid, and heat it for about half an hour in an evaporating dish containing water, by placing a small Bunsen-flame under the dish. Extinguish the flame, and then take out the paper-coil. The coil is now free from all matter soluble in ether, and is ready for use.

An alternative method is given in par. **588**, whereby the extractive matter is estimated and is allowed for in the fat residue at the end of the process.

Mix the milk well by shaking, determine its density (**23–28**), and take out 5 c.c. by means of a pipette. Allow this to flow slowly over the coil of paper, so as to wet the whole, the coil meanwhile being suspended on a glass rod. Now suspend the coil in the steam-oven for about an hour. The water is thus driven off.

The following method of preparing the paper-coil for extraction is also satisfactory. Pin the end of one of the paper strips to the edge of the bench, so that the strip hangs vertically in the air. Allow 5 c.c. of the milk to slowly drop upon the paper and to be absorbed by it. Remove the last portions of the milk from the point of the pipette by rubbing the point against the dry part of the paper. Allow the strip to hang until it is quite dry, hastening the drying process, if necessary, by holding the strip near the side of a steam-oven. The paper strip is then rolled into a coil, as is described above.

Next place the dry coil in the Soxhlet-extractor; pour about 100 c.c. of anhydrous ether into the weighed flask; and heat the flask in the dish of water sufficiently to keep the ether boiling. Maintain the heat until the ether has syphoned over at least twelve times.

If any suspended matter is present in the tared flask, the ethereal solution must be filtered into a second tared flask; the filter is then washed with ether, and the washings are added to the flask before distilling off the ether.

Then distil off the ether, as far as possible, from the flask; and dry the fat-residue by heating the flask upon the water-bath, and finally in the steam-oven. As soon as the weight of the flask containing the fat is constant, the amount of the fat is found by subtracting the weight of the flask. The weight of the 5 c.c. of milk originally used is calculated from the density of the milk.

591. The Other Principal Constituents of the Milk are not estimated directly, but their amounts are calculated from the results already obtained, as is described below.

(a). **Estimation of Water.**—The water in the milk is estimated by difference. The percentage of milk solids (**582**), when subtracted from 100, gives the percentage of water.

(b). **Estimation of the "Solids not Fat."**—The percentage of "solids not fat" is obtained by subtracting the percentage of fat (584–590) from the percentage of milk solids (582).

(c). **Estimation of Fat by Calculation.**—As a check upon the results obtained by the direct analysis of milk, an indirect method by calculation may be used with great advantage. It is based upon the following considerations.

The specific gravity of milk depends upon the amount of fat and of "solids not fat" present, the former tending to lower the specific gravity, the latter to raise it. From a number of analyses various observers have constructed formulæ expressing these relations.

One of these formulæ, which is adapted to the Adams process of fat extraction, is that of Hehner and Richmond; it is the following:—

$$F = 0{\cdot}859\ T - 0{\cdot}2186\ G,$$

in which F represents the percentage of fat, T the percentage of total solids, and G the number by which the specific gravity of the milk exceeds 1000 (sp. gr. of water being 1000). For poor skimmed milks a correction must be subtracted from the above formula of $0{\cdot}05\left(\frac{G}{T} - 2{\cdot}5\right)$.

Example.—Thus in a milk which contained 12·5 per cent. of total solids, and had a specific gravity of 1030, the percentage of fat $= 12{\cdot}5 \times 0{\cdot}859 - 0{\cdot}2186 \times 30 = 4{\cdot}38$.

592. **Remarks on the Results of Milk Analysis.**—The results of the analysis of milk may either be returned as grams per 100 c.c., or as percentage weights. If the latter method is adopted, the specific gravity of the well-mixed milk at 15°·5 C. is taken (23–28); from this the weights of the volumes of milk which have been used can be calculated, and the results can therefore be calculated as percentage weights. An alternative method is to weigh the separate portions of the milk used in the analysis instead of measuring them.

The following numbers are the averages of a large number of percentage results obtained from the analyses of genuine milk sold in this country:—

	Country-milk.	Town-milk.	Average-milk.
Water, . .	87·55	85·94	87·1
Fat, . . .	3·07	4·00	4·1
Casein, . .	4·04	5·01	} 8·8
Milk-sugar, .	4·63	4·31	
Ash, . . .	0·71	0·74	
	100·00	100·00	100·0

The most common adulterant of milk is water. The addition of water reduces the amount of "solids not fat." The "solids not fat" in genuine whole milk should not be less than 8·5 per cent. This number, however, represents a milk of very poor quality, and 9 per cent. is sometimes the minimum limit accepted.

The quality of the milk may also be reduced by the removal of fat in the form of cream.

The amount of fat present in the milk should not be less than 3 per cent. It may be noted that the amount of "fat" in genuine milk tends to rise in the winter months, reaching a maximum in November.

Taking the above average normal percentages of "fat" and of "solids not fat" as standards, the extent of adulteration with water, or of impoverishment by the removal of fat, may be calculated.

Thus, if a is the percentage of "solids not fat" in a sample of watered milk, the number of grams of pure milk contained in 100 grams of the sample will be $\frac{100}{8{\cdot}5} \times a$.

Also, if b is the percentage of fat, the number of grams of fat which have been removed by skimming 100 grams of the unadulterated "whole milk" would be $\frac{3a}{8{\cdot}5} - b$.

Analysis of Butter.

593. The estimations which are usually made in butter are the following:—water, fat, curd, and salt. In case the butter is to be tested for foreign fats, a further examination is necessary, such as is described in paragraphs **599–601.**

594. Estimation of Water.—Weigh out accurately about 5 grams of the butter into a weighed porcelain dish; and heat it in the steam-oven, until no globules of water can be seen below the fat, and until the weight becomes constant. The loss of weight represents the water.

This operation may be shortened by heating the butter in an air-oven to a temperature of 110° C.

595. Estimation of Curd and Salt.—Melt the dry butter (**594**), and treat it with about 10 c.c. of ether. Pour off the ethereal solution through a tared filter. Treat the residue again with ether; then transfer it to the filter and continue to wash it with ether, until a few drops of the ether give no residue when they are evaporated to dryness on a watch-glass. Then dry the filter and its contents in the steam-oven, until their weight becomes constant. The weight of the residue represents the quantity of curd and salt in the weight of butter taken (**594**).

The ether solution may be reserved for the direct estimation of the fat (**597**).

596. Estimation of Ash.—Transfer the dried filter and its contents (**595**) to a weighed platinum crucible, and ignite them at as low a temperature as possible, until the residue is white in colour and its weight is constant.

The residue should consist almost wholly of salt. In order to ascertain if this is the case, dissolve it in water and titrate the solution with standard silver nitrate solution, as is described in paragraph **304.**

597. Estimation of Fat.—The fat may be estimated either

by difference or directly. The estimation by difference is the more exact method.

If the fat is to be estimated by difference, its percentage is found by subtracting the sum of the percentages of water, curd, and salt (594, 595) from 100.

If the fat is to be estimated directly, the ethereal solution and washings from par. 595 are transferred to a weighed flask, and the ether is distilled off as far as possible. The flask containing the residue of fat is then heated for some time on the water-bath, and is finally dried in the steam-oven until its weight is constant.

598. Remarks on the Results of Butter Analysis.—A few percentage analyses of unadulterated butters are appended.

Water, . . .	6·5	9·7	12·4	11·2
Curd, . . .	2·4	3·5	1·5	3·1
Salt, . . .	1·6	2·1	1·0	2·0
Fat, . . .	89·5	84·7	85·1	83·7

Hehner states that the percentage of water present in well-made butter of good quality is not as a rule more than 13, or less than 11. A proportion exceeding 17 per cent. would indicate either careless making or intentional adulteration.

The percentages of curd and salt together should amount to about 2·5 per cent.: and although this weight may be considerably higher, it should never reach 8 per cent.

The fat, which averages from 85 to 87 per cent., should never fall below 80 per cent.

Detection of Foreign Fats in Butter.

Three methods for detecting the adulteration of butter by foreign fats, and for ascertaining the extent of the adulteration, are given below.

They are Reichert's method (599), Hehner's method (600), and Koettstorfer's method (601). The degree of rancidity of butter may also be estimated by the last-named method. See par. 602.

599. Reichert's Method of Detecting Foreign Fats in Butter.—This method is based upon the fact, that genuine butter furnishes more than 4 per cent. of volatile fatty acids; whereas other fats either furnish no volatile acid, or else a very much less proportion than butter does.

A modification of Reichert's original method is described below. The following preliminary preparations are necessary.

(a). *Caustic Soda Solution.*—Dissolve 50 grams of caustic soda in 50 c.c. of water, and let the liquid stand until it becomes quite clear. This solution will be free from carbonate, since sodium carbonate is quite insoluble in a solution containing 50 per cent. of sodium hydrate.

(b). *Dilute Sulphuric Acid* of such strength that 5 c.c. are more than sufficient to neutralise 1·5 c.c. of the above caustic soda solution.

(c). *Deci-normal Solution of Barium Hydrate.*—This solution is preferred for the final titration of the volatile in fatty acids, since it can contain no soluble carbonate. If carbon dioxide were liberated from carbonate during the titration it would seriously interfere with the process.

(d). *Preparation of "Butter-Fat."*—Prepare some butter-fat, free from moisture, salt, and curd, in the following way.

Melt some of the butter in a dish. When it is clear, filter off the water, curd, and salt through a dry filter, keeping the fat in a fused condition during filtration by means of a hot-water funnel (fig. 55, p. 71). Care must be taken that none of the water is poured out upon the filter. The filtered liquid fat should be perfectly clear and transparent. This will in future be termed "butter-fat," to distinguish it from the unclarified butter.

Process of Estimation.—When the "butter-fat" (d) is cold, weigh out 2·5 grams into a dry flask, capable of holding about 200 c.c. Add about 10 c.c. of alcohol, and then 1·5 c.c. of the solution of caustic soda (a). At once close the flask with an india-rubber cork, and gently shake the con-

tents until they have become quite clear. Allow the mixture to stand at a gentle heat for about ten minutes to complete the saponification.

Now remove the india-rubber stopper, and replace it by a perforated cork, bearing a short piece of narrow glass tubing open at both ends. Then heat the flask upon the water-bath, so as to evaporate the alcohol. The narrow glass tube prevents the entry of any carbon dioxide from the air, the absorption of which would ultimately raise the results obtained.

When the alcohol has been driven off, add 70 c.c. of boiling distilled water, which has been freed from carbon dioxide by being boiled for at least twenty minutes, and once more close the flask by the rubber stopper. As soon as the soap has been dissolved by the hot water, add 5 c.c. of the dilute sulphuric acid (b). Shake the contents of the flask well, drop a few pieces of broken clay-pipe into the flask, and distil through a Liebig-condenser at such a rate, that 50 c.c. of distillate are collected in about a quarter of an hour. It is important that this distillation should not actually begin until the fatty acids in the flask are melted to a clear yellowish oily fluid.

The acid distillate is filtered through a filter-paper, which has previously been well-washed with the distilled water which has been boiled until it is free from carbonic acid. The filter is then washed until it is free from acid, and the well-mixed filtrate and washings are titrated with the deci-normal baryta solution (c), phenol-phthalein (228) being used as an indicator.

If the butter-fat is genuine, the 50 c.c. of distillate will usually require for neutralisation about 13 c.c. of the deci-normal barium hydrate solution: the quantity will rarely be less than 12·5 c.c. Butter made from the milk of single cows not unfrequently gives lower results, especially when the cows are near the end of their period of lactation. On the other hand, butters produced in Egypt, Australia, and New Zealand usually require from 15 to 16 c.c. Every sample of market-butter,

which has been made from the mixed milk of a number of cows and requires less than 12·5 c.c., should therefore be looked upon with suspicion; and if the result obtained by this method is confirmed by other means, the sample must be considered to be adulterated.

The volatile acid contained in the 50 c.c. of distillate represents almost accurately 83 per cent. of the total quantity of volatile fatty acids contained in the butter-fat. Hence by multiplying the number of c.c. of deci-normal solution used for 2·5 grams of butter-fat by the factor 0·424, the percentage of total volatile acids present, calculated as butyric acid ($C_4H_8O_2$), is approximately obtained.

The above factor is derived thus:—Since the molecular weight of butyric acid is 88, each c.c. of deci-normal baryta solution corresponds to 0·0088 gram of butyric acid: and since 25 grams of butter-fat were used, the percentage of butyric acid $= \left(n \times 0{\cdot}0088 \times \frac{100}{83}\right) \times 40$, where n is the number of c.c. of baryta solution used.

The Process is more Rapid and Simple if it is modified as follows.

Caustic Soda Solution.—Dissolve 50 grams of caustic soda, dilute to 100 c.c., and filter through a toughened filter. Add this to 500 grams of pure glycerine, and stir well.

Process of Estimation.—Weigh 5 grams of the butter-fat into a wide-mouthed flask, add 10 c.c. of the glycerine solution, and heat on a sand-bath until frothing ceases and the solution becomes clear. Allow the liquid to cool somewhat, and then add gradually 95 c.c. of freshly-boiled distilled water, guarding against loss by frothing.

Now add 50 c.c. of normal sulphuric acid (**236**), drop in some pieces of pumice, connect the flask with a condenser, and commence the distillation as soon as the layer of fatty acids has become quite clear. This process has been described above.

Collect 110 c.c. by distillation; filter off 100 c.c. of this distillate through a dry filter, and titrate the acid in this by deci-normal barium hydrate solution (c), using phenol-phthalein as an indicator (**228**). Add to this result one-tenth of the number of c.c. of barium hydrate solution used.

Process of Calculation.—If N represents the number of c.c. of deci-normal barium hydrate solution required for the neutralisation of the fatty acids, and n represents the volume in c.c. of the standard barium

hydrate solution required by the distillate in a blank estimation, then since 5 grams of normal butter-fat require 26 c.c., the

$$\text{Percentage of foreign fats} = \frac{(26 - N) \times 100}{26 - n}$$

Adulteration with Foreign Fats.—The following statement shows that the volatile fatty acids, which are derived from equal weights of other ordinary fats, require a far smaller volume of the standard alkali to neutralise them than is the case with butter-fat.

The volume in c.c. of deci-normal barium hydrate solution, which is required for neutralising the volatile fatty acids from 2·5 grams of the following fats, is for

Genuine butter, . . .	14·32
Cocoa-nut fat, . . .	3·6
Beef-fat, ...	0·25
Lard, ...	0·30
Margarine, ...	0·2 to 1·6

These numbers differ so widely from that obtained from butter-fat, that they furnish a means not only of detecting the admixture of foreign fats with the butter, but of calculating its amount.

In calculating the percentage amount of adulteration in the butter-fat, the lowest number of c.c. required by 2·5 grams of genuine butter, 12·5, should be taken, whilst for margarine the highest number, 1·6, is selected.

Thus, if x c.c. of the barium hydrate solution are required by a sample of butter-fat, the percentage of pure butter-fat in the sample will be $\frac{x - 1{\cdot}6}{12{\cdot}5 - 1{\cdot}6} \times 100 = \frac{100(x - 1{\cdot}6)}{10{\cdot}9}$.

600. Hehner's Method of Detecting Foreign Fats in Butter.—This method depends upon the fact, that butter-fat contains a smaller proportion of fatty acids insoluble in water than other fats do. Hence, by estimating the amount of insoluble fatty acids in a sample of butter, the presence of foreign fats may be detected, and the proportion in which they are present may be calculated.

The Process.—Free the butter from moisture, curd, and salt (599, d). Then weigh accurately about 4 grams into an evaporating dish, about 6 inches in diameter. Fuse the fat on the water-bath, and add from 5 to 10 c.c. of a saturated solution of potassium hydrate in alcohol. The fat will be at once saponified. Now add a few drops of water, and if any fat separates out, add more alcohol and continue the heating.

Dilute the soap-solution thus formed with water, and then evaporate until the smell of alcohol is no longer perceptible. Dissolve the soap, which will have partly separated out, in water; and add dilute hydrochloric acid until the solution strongly reddens litmus-paper. Then heat the dish for about half an hour on the water-bath. The fatty acids will form an oily layer above the aqueous solution, which should itself be almost clear.

Separation and Washing of the Fatty Acids.—Now rinse out a butter-flask (fig. 79) with hot water, and transfer the fatty acids together with the liquid to the flask, reserving the dish. Allow the aqueous liquid to flow away by opening the stop-cock (*a*), leaving the melted fatty acids in the flask. Pour hot water into the flask, and shake it well with the fatty acids; then allow the water to flow away again. Repeat this process of washing until the washing-water is no longer acid in reaction.

FIG. 79.

Now carefully open the stop-cock, and allow the fatty acids to just reach the lower end of the tube (*a*), and remove the drop of water from beneath the fat by touching it with filter-paper.

Then allow the whole of the fat to flow into a weighed glass dish. Rinse out the dish, which was used for the saponification, with a little ether. Pour this liquid into the butter-flask, and after shaking it round in the flask, allow it to flow through the tube (*a*) into the weighed dish. Rinse the butter-flask twice with fresh small portions of ether, and add these to the

liquid in the glass dish. Evaporate the ether by gentle heat, and heat the dish and residue in the steam-oven for a short time, and cool.

If a drop of water is seen beneath the fat, cut out a circular piece of fat with a sharp pen-knife, so as to be able to reach the water and absorb it by a piece of filter-paper. Then place the dish in the water-oven, heat it for two hours, and weigh it when it is cold. Repeat these processes, until the difference between two consecutive weighings amounts to 1 or 2 milligrams only; the fat may then be considered as dry, and the final weighing is accepted.

The Presence of Admixed Foreign Fats may be ascertained, and their amount may be found, from the percentage of insoluble fatty acids which is thus obtained.

Since animal fats contain on the average 95·5 per cent. of insoluble fatty acids, and butter-fat contains on an average only 87·5 per cent., 100 parts of foreign fat contain 8 parts of insoluble fatty acids more than 100 parts of butter do. Hence if (a) represents the percentage of insoluble fatty acids found, then the amount of foreign fat present in 100 parts of the butter-fat $= \frac{100(a - 87{\cdot}5)}{8} = 12{\cdot}5(a - 87{\cdot}5)$.

Example.—In a particular estimation the butter-fat contained 93·5 per cent. of insoluble fatty acids; hence the amount of adulteration in 100 parts of the fat $= 12{\cdot}5(93{\cdot}5 - 87{\cdot}5) = 12{\cdot}5 \times 6 = 75$. But the butter sample contained 15 per cent. of water, curd, and salt, and 85 per cent. of butter-fat: therefore the percentage of adulteration in the butter $= \frac{75 \times 85}{100} = 63{\cdot}75$, or the percentage of real butter present $= 36{\cdot}25$.

Note.—Although the percentage of insoluble fatty acids in butter is, as a rule, 87·5, genuine butter has been found to contain 88·5, and even 89 per cent.

601. Koettstorfer's method of detecting Foreign Fats in Butter.—This method depends upon the great difference between the molecular weights of different fatty acids. This difference is made evident, when the weight of each acid

required to neutralise a certain weight of potassium hydrate is determined.

While the molecular weights of the fatty acids in most natural fats are high, and do not widely differ one from another; butter alone contains some quantity of fatty acids of comparatively low molecular weight, containing not more than ten atoms of carbon in their molecules.

Hence the alkali-neutralising power of a certain weight of butter will be greater than that of an equal weight of any other natural fat; and its neutralising power will be diminished by the admixture of other fats.

The method founded on the above facts is simple and rapid. The solutions required are the following.

(a). *Alcoholic Solution of Potassium Hydrate.* — Thirty-two grams of caustic potash are dissolved in 1 litre of 94 per cent. alcohol. Since this solution is subject to change by oxidation, it should be prepared in small quantity only, and must not be stored for any length of time. It must be titrated with standard acid each time it is used.

(b). *Semi-Normal Hydrochloric Acid Solution*, made by diluting normal hydrochloric acid solution (**240**) with its own volume of water.

(c). *Phenol-phthalein Solution:* very dilute solution in alcohol (**228**).

The Process of Estimation.—The butter is first purified by fusion and filtration (**599, d**).

About 3 grams of this "butter-fat" are accurately weighed into a flask holding about 250 c.c.; 25 c.c. of the potassium hydrate solution (a) are then added, and the contents of the flask are heated for about 15 minutes under a reflux condenser. Complete saponification is thus effected. A few drops of the phenol-phthalein solution (c) are then added, and the free alkali is titrated with the hydrochloric acid solution (b). The change of colour to yellow sharply indicates the end of the reaction.

Meanwhile 25 c.c. of the alcoholic potash solution (**a**) are treated in precisely the same way as is described above, and are finally titrated with the standard acid.

The difference between the number of c.c. of acid which have been required in these two titrations is calculated; and this is taken as representing the volume of semi-normal potassium hydrate solution, which has been neutralised by the fatty acids of the butter-fat which was used in the experiment. This number of c.c. is multiplied by 0·028 to obtain the weight of potassium hydrate which has been neutralised by the butter-fat. From this result the number of milligrams of potassium hydrate is calculated which would be neutralised by 1 gram of the butter-fat.

Pure butter-fat, when treated in this way, gives a number between 221·5 and 233. Both oleo-margarine and lard, the common adulterants of butter, give about 195·5.

If the number which is yielded by a sample of butter-fat is below 221·5, the butter has been adulterated. The probable percentage amount of adulteration can then be calculated from the statement $(227{\cdot}25 - n) \times 3{\cdot}17$; in which n is the number obtained from the sample analysed, and 227·25 is the mean number for pure butter-fat.

Example.—In a particular estimation 1·76 grams of the butter-fat were used.

The blank titration of 25 c.c. of the KHO solution required 20·4 c.c. of standard acid.

The titration of 25 c.c. of the KHO solution, which had been heated with the butter-fat, required 6·0 c.c. of acid.

Therefore the fatty acids were equivalent to $20{\cdot}4 - 6{\cdot}0 = 14{\cdot}4$ c.c. of semi-normal acid, and would therefore neutralise 14·4 c.c. of semi-normal KHO solution.

One gram of the butter-fat would therefore neutralise $\frac{14{\cdot}4}{1{\cdot}76} = 8{\cdot}18$ c.c. of semi-normal KHO solution, $= 8{\cdot}18 \times 0{\cdot}028 = 229{\cdot}04$ milligrams of KHO.

And since 1 gram of pure butter-fat neutralises from 221 to 233 milligrams of KOH, the sample of butter under examination was not adulterated with foreign fats.

602. Estimation of Rancidity in Butter.—The above method offers a means of determining the degree of rancidity in butter, by estimating

the amount of free acid present in it. From 3 to 10 grams of the "butter-fat" (599, d) are weighed into a flask of about 50 c.c. capacity. Some ether is then freed from acidity, by adding first some phenolphthalein solution (601, c), and then the alcoholic caustic potash solution (601, a) until the violet colour is just permanent. This ether is then added in sufficient quantity to dissolve the butter-fat. The acid in the butter-fat solution is then titrated with the alcoholic potash solution, the value of which has been ascertained by means of semi-normal hydrochloric acid (601, b).

The number of c.c. of normal potash solution required by 100 grams of palatable rancid butter-fat varies from 1 to 8, giving an average of 4. In exceptional cases 15, 26, and even 41·6 c.c. have been required, but this last corresponds to an intolerable degree of rancidity.

Partial Analysis of Beer and Wine.

603. The usual estimations which are made in the chemical examination of a sample of beer are those of alcohol, acidity, and of materials other than alcohol dissolved in the beer.

For excise purposes it is necessary to ascertain the "original gravity" of the beer. This indicates the relative amount of solid matter dissolved in the "wort" before it is fermented.

604. Estimation of the Alcohol in Beer and Wine.—About 750 c.c. of the liquid is freed from the greater part of the carbon dioxide dissolved in it. For this purpose the liquid may be filtered; or it may be "tossed," by pouring it backwards and forwards from one vessel to another.

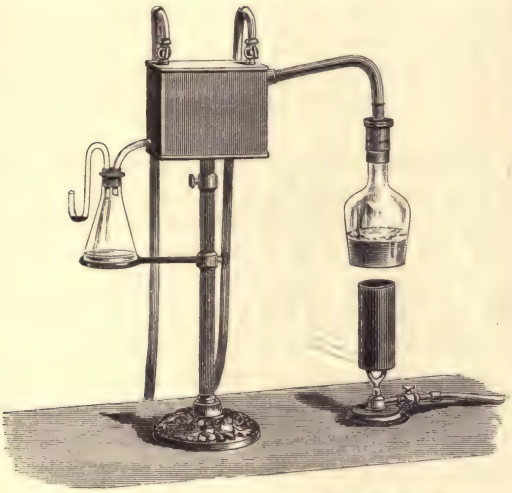
The liquid is then distilled, either in a flask attached to an ordinary Liebig-condenser, or in the apparatus which is shown in fig. 80. A vertical condenser with glass spiral inner-tube and broad glass jacket is now frequently used in place of the older metal still, which is shown in the figure.

This apparatus consists of a flask about 1 litre in capacity, upon the neck of which is cemented a brass tube bearing a screw-thread on its outside. This fits into a screw, which is

on the interior of a brass cap connected with the condensing-tube. A rubber washer, which is inserted between the top of the flask and the under surface of the cap, makes the connection of the flask with the condensing-tube perfectly tight when it is screwed up.

In the centre of the figure is seen the metal condensing-box, and to the left the flask for receiving the distillate. A cork, pierced with two holes, is fitted into the neck of this flask. Through one hole passes the tube conveying the distillate, through the other is fitted a bent tube open at both

FIG. 80.



ends; the lower bend contains a globule of mercury, which prevents the loss of alcohol vapour by diffusion. The cold water supply for condensing the spirit, and the overflow of heated water, are conveyed by tubes which are seen at the back of the condenser.

605. *The Process of Estimation.*—Measure 250 c.c. of the "tossed" liquid into the flask to the right. Connect the flask with the condenser and receiver. Then heat the flask gently with the flame of an Argand-burner.

When about two-thirds of the liquid have distilled over, transfer the distillate to a measuring-flask, make it up to the original volume of the liquid with distilled water, and mix well. Then take the specific gravity of this liquid at 15°·5 C., either by direct weighing, or by means of a delicate hydrometer (23–28).

The amount of proof-spirit and of absolute alcohol present in the liquid may then be ascertained from the specific gravity, by reference to the Alcohol Tables in the Appendix (776, 777) in which the specific gravity of water is taken as 1000. Fuller Tables by Hehner are published.

The residual liquid in the distillation-flask is allowed to cool; it is then diluted to the original volume, and its specific gravity is taken at 15°·5 C. The number thus obtained is used in calculating the "original gravity" of the beer.

606. Estimation of the "Original Gravity" of Beer.—As has been already explained, the "original gravity" of a beer is the gravity of the wort before fermentation.

During the process of fermentation, a portion of the saccharine matter is converted into alcohol and carbon dioxide. Therefore beer has a lower specific gravity than the wort from which it has been brewed.

In order to determine the original gravity of the wort, the alcohol is separated from the beer by distillation, and the specific gravity of the distillate is determined as is directed above (605). The gravity of the wort required to produce this specific gravity is then ascertained by reference to Table I. below, in which the degree of "spirit indication" is the difference between 1000 and the specific gravity of the alcoholic distillate (sp. gr. of water = 1000).

The number thus obtained is then added to the specific gravity of the liquid, which was produced by diluting the residue left in the distillation-flask (605) to 250 c.c. The resulting number represents the original specific gravity of the wort.

TABLE I.—*Spirit Indication, with corresponding Degrees of Gravity lost in Malt Worts, by the "Distillation Process."*

Degrees of Spirit Indication.	·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0.8	0·9
0	...	0·3	0·6	0·9	1·2	1·5	1·8	2·1	2·4	2·7
1	3·0	3·3	3·7	4·1	4·4	4·8	5·1	5·5	5·9	6·2
2	6·6	7·0	7·4	7·8	8·2	8·6	9·0	9·4	9·8	10·2
3	10·7	11·1	11·5	12·0	12·4	12·9	13·3	13·8	14·2	14·7
4	15·1	15·5	16·0	16·4	16·8	17·3	17·7	18·2	18·6	19·1
5	19·5	19·9	20·4	20·9	21·3	21·8	22·2	22·7	23·1	23·6
6	24·1	24·6	25·0	25·5	26·0	26·4	26·9	27·4	27 8	28·3
7	28·8	29·2	29·7	30·2	30·7	31·2	31·7	32·2	32·7	33·2
8	33·7	34·3	34·8	35·4	35·9	36·5	37·0	37·5	38·0	38·6
9	39·1	39·7	40·2	40·7	41·2	41·7	42·2	42·7	43·2	43·7
10	44·2	44 7	45·1	45·6	46·0	46·5	47·0	47·5	48·0	48·5
11	49·0	49·6	50·1	50·6	51·2	51·7	52·2	52·7	53·3	53·8
12	54·3	54·9	55·4	55·9	56·4	56·9	57·4	57·9	58·4	58·9
13	59·4	60·0	60·5	61·1	61·6	62·2	62·7	63·3	63·8	64·3
14	64·8	65·4	65·9	66·5	67·1	67·6	68·2	68·7	69·3	69·9
15	70·5	71·1	71·7	72·3	72·9	73·5	74·1	74·7	75·3	75·9
16	76·5	...	...	...	...	...	...	...	...	...

The acidity which has been produced during fermentation, is estimated and allowed for as follows.

The acidity of the tossed beer is ascertained by titrating 100 c.c., or more correctly 100 grams, of the beer with semi-normal sodium hydrate solution, using litmus-paper as an indicator. From this result the amount of acetic acid is calculated, assuming that each c.c. of the semi-normal sodium hydrate solution corresponds to 0·03 gram of acetic acid.

TABLE II.—*For Ascertaining the Value of the Acetic Acid.*

Excess per cent. of Acetic Acid in the Beer.	Corresponding Degrees of "Spirit Indication."									
	0·00	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·08	0·09
0·0	...	0·02	0·04	0·06	0·07	0·08	0·09	0·11	0·12	0·13
0·1	0·14	0·15	0·17	0·18	0·19	0·21	0·22	0·23	0·24	0·26
0·2	0·27	0·28	0·29	0·31	0·32	0·33	0·34	0·35	0·37	0·38
0·3	0·39	0·40	0·42	0·43	0·44	0·46	0·47	0·48	0·49	0·51
0·4	0·52	0·53	0·55	0·56	0·57	0·59	0·60	0·61	0·62	0·64
0·5	0·65	0·66	0·67	0·69	0·70	0·71	0·72	0·73	0·75	0·76
0·6	0·77	0·78	0·80	0·81	0·82	0·84	0·85	0·86	0·87	0·89
0·7	0·90	0·91	0·93	0·94	0·95	0·97	0·98	0·99	1·00	1·02
0·8	1·03	1·04	1·05	1·07	1·08	1·09	1·10	1·11	1·13	1·14
0·9	1·15	1·16	1·18	1·19	1·21	1·22	1·23	1·25	1·26	1·28
1·0	1·29	1·31	1·33	1·35	1·36	1·37	1·38	1·40	1·41	1·42

The following statement illustrates the method of calculating the "original gravity" of a sample of beer.

Example.—If 1000 be taken as the specific gravity of water, the gravity of the distillate will be less than 1000; suppose it to be 989·33. This number is deducted from 1000, and furnishes the "spirit indication," which in this case is 10·67. On referring to Table I., it will be seen that the corresponding number is 47·35. This represents the number of degrees of gravity which were lost in the production of the spirit during fermentation.

If the specific gravity of the diluted residue from the distillation was 1023·42, and no acid was detected in the beer, the original gravity of the beer would be $1023{\cdot}42 + 47{\cdot}35 = 1070{\cdot}77$.

Suppose, however, that the acidity was such, that 100 grams of the beer required 11 c.c. of semi-normal NaHO for neutralisation; then the percentage of acid would be $11 \times 0{\cdot}03 = 0{\cdot}33$. But the average percentage of acidity in unfermented wort amounts to 0·1 per cent., therefore 0·23 only of the acid will be due to oxidation of the alcohol. Referring to Table II., it is seen that the spirit indication corresponding to 0·23 of acid is 0·31, therefore the total spirit indication will be $10{\cdot}67 + 0{\cdot}31 = 10{\cdot}98$. On referring to Table I., it will be seen that the gravity lost by the formation of alcohol in the beer corresponding to this number is 48·9. Hence the original gravity would be $1023{\cdot}42 + 48{\cdot}9 = 1072{\cdot}32$.

Analysis of Sugar.

In the chemical examination of sugar, four estimations are usually made; they are those of moisture, ash, cane-sugar, and invert-sugar or glucose. Moist brown sugar will be found the most suitable kind of sugar to analyse for practice in the method.

607. Estimation of Moisture.—Weigh out accurately about 4 grams of the sugar in the watch-glasses with clip; and heat this in the steam-oven, until the weight becomes constant.

608. Estimation of Ash.—Transfer the dried sugar (**607**), little by little, to a platinum crucible; and incinerate each part, as it is added, at as low a temperature as possible.

The mass will fuse and swell as the heating proceeds. Take care that the sugar does not extend over the edge of the crucible.

When the charred mass has assumed the appearance of coke, gently stir it from time to time with a thick platinum wire or spatula, or with a thin glass rod, so as to assist the combustion of the carbon. Finely powdered ammonium nitrate may be added to the ash to facilitate the complete combustion of the carbon. As soon as the ash is free from black particles, allow the crucible to cool, and weigh the ash.

609. Estimation of the Sugar.—The process described below depends upon a chemical reaction. It should be stated, however, that the most accurate estimation of sugar is made by means of the polariscope.

Before the cane-sugar, $C_{12}H_{22}O_{11}$, is estimated chemically, it is usually converted into glucose, $C_6H_{12}O_6$, by digesting it with a dilute acid :—$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$.

The glucose is then estimated by heating it with an alkaline solution of copper, known as Fehling-solution. The blue colour of this solution disappears during the reaction, while red cuprous oxide is precipitated. Allowance is made in calculating the result, for the increase of weight which the cane-sugar has undergone by its combination with the elements of water.

In practice the total amount of glucose, both that derived from the cane-sugar and that originally present in the sugar, is first estimated. The glucose which was originally present as such in the sugar is then also estimated. The difference between these two estimations gives the amount of glucose derived from the cane-sugar.

It should be noted that solutions containing from 0·5 to 1 per cent. of glucose give the most consistent and accurate results in this process of estimation. If the preliminary analyses show that the solution is much weaker or much stronger than this, the amount of sugar in solution should be altered accordingly.

610. *Preparation of the Fehling Solution.*—Weigh out 69·28 grams of pure recrystallised copper sulphate. Dissolve this in water, adding a few drops of H_2SO_4 if the solution is not perfectly clear. Add to this a solution containing 350 grams of Rochelle salt and 100 grams of sodium hydrate. The mixed solutions are made up to 1 litre, and 25 c.c. of this Fehling-solution are used for each estimation.

The Fehling-solution, as thus prepared, gradually undergoes chemical change and alters in strength when it is kept. This may be obviated by dissolving the copper sulphate in a litre of water, and dissolving the Rochelle salt and the sodium hydrate in another litre of water. These solutions are kept in separate bottles, and 25 c.c. of each of them are mixed together immediately before use.

As a rule 25 c.c. of the original Fehling-solution, or 50 c.c. of the mixed solutions, correspond to 0·25 gram of glucose; but it is always necessary to standardise the solution.

611. *Standardisation of the Fehling Solution.*—In order to standardise the solution, weigh out 5 grams of pure crystallised cane-sugar. Place it in a bottle with about 50 c.c. of water and 1 c.c. of strong hydrochloric acid. Then close the bottle with a sound cork, and bind the cork down with wire. Now immerse the bottle in the water-bath, and digest it for half an hour at 100° C. The cane-sugar is thus completely converted into glucose. Neutralise the cold liquid with sodium hydrate solution, and make it up to 500 c.c. with distilled water.

Fill a burette to the zero with this sugar solution. Measure 25 c.c. of the Fehling-solution into a porcelain dish 6 inches in diameter; or, if the copper and caustic soda solutions are kept in separate bottles, mix together 25 c.c. of each of them in the dish. Make up the solution to 200 c.c. with water, and add nearly the whole of the sugar solution from the burette in portions of about 5 c.c. Boil the liquid for two minutes after each addition of the sugar solution. As soon as the deep blue colour of the copper

solution begins to fade, add the sugar solution cautiously, still boiling the liquid after each addition.

As the final disappearance of the blue colour approaches, the red precipitate of Cu_2O will somewhat obscure the colour of the copper solution. If, however, a few seconds are allowed for the subsidence of the precipitate, and the dish is slightly tilted, the colour of the solution is readily seen.

The exact point of complete precipitation of the copper is readily ascertained, even if the liquid is coloured, by passing a few drops of the liquid through a *small* filter; the clear filtrate is then tested for copper by adding an excess of acetic acid, and one drop of potassium ferrocyanide solution. If any copper is still present in the solution, a brown colour will be seen. The cautious addition of the sugar solution, followed by boiling, must be continued until the ferrocyanide reaction does not occur.

Now ascertain the strength of the Fehling-solution with greater accuracy, by repeating the titration, and adding nearly the whole of the requisite quantity of the sugar solution within half a c.c. Boil the liquid for two minutes; and finally add the sugar solution very cautiously, boiling after each addition. Two such titrations should not differ by more than one-fifth of a c.c. It is necessary to carry out this final titration rapidly, in order to minimise the oxidation which occurs by contact with the air.

612. Estimation of the "Invert Sugar," or Glucose, originally present in the Sugar.—Dissolve 10 grams of the sugar in water, and make this solution up to 200 c.c. Fill a burette to zero with this solution. Then measure out 25 c.c. of the Fehling-solution (**610**) into a glazed porcelain dish, about 6 inches in diameter, and dilute to 200 c.c. Titrate by adding the sugar solution to the Fehling-solution (**611**).

If the amount of glucose present is very small, only 5 c.c. of Fehling-solution should be used.

The percentage weight of glucose, present in the sugar, can be readily calculated; since the glucose-value of the Fehling-solution is known.

613. Estimation of the Cane-sugar.—Weigh out 1 gram of the cane-sugar accurately, and dissolve it in water. Dilute the solution to about 100 c.c. with distilled water. Place this solution in a bottle. Add 1 c.c. of strong hydrochloric acid and cork the bottle, binding down the cork with wire. Heat the bottle in the water-bath for half an hour. Then neutralise the liquid, make it up to 200 c.c., and titrate it with the Fehling-solution, as is described above (**611**).

Subtract the percentage of glucose found (**612**), from the percentage calculated from the present estimation. The percentage of glucose derived from the cane-sugar is thus obtained.

From this the percentage weight of cane-sugar can be calculated. For since the relative weights of cane-sugar, and of the glucose which it furnishes by inversion, are 342 : 360 ; it follows that, if the weight of the glucose found is multiplied by $\frac{342}{360}$, or by 0·95, the weight of the cane-sugar, from which the glucose had been derived, is obtained.

Example.—In an estimation of the amount of glucose and cane-sugar in a sample of moist-sugar, the following results were obtained.

For the estimation of the *Invert Sugar* 10 grams of the sugar were dissolved in water, and the solution was made up to 200 c.c.

Twenty-five c.c. of Fehling-solution, equal to 0·25 gram of glucose, required 60 c.c. of the sugar solution.

Hence the percentage of invert-sugar $= \frac{200 \times 100 \times 0{\cdot}25}{10 \times 60} = 8{\cdot}33$.

For the estimation of the *Total Sugar*, 2 grams of the sugar were inverted, and made up to 200 c.c.

Twenty-five c.c. of Fehling-solution required 27·5 of this sugar solution.

Hence the total percentage of sugar, as glucose, $= \frac{200 \times 100 \times 0{\cdot}25}{2 \times 27{\cdot}5}$

$= 90{\cdot}91$.

Hence the percentage of glucose equivalent to the cane-sugar $= 90{\cdot}91 - 8{\cdot}33 = 82{\cdot}58$; and the percentage of cane-sugar $= 82{\cdot}58 \times 0{\cdot}95 = 78{\cdot}45$.

Partial Analysis of Tea.

614. The value of tea depends upon its natural quality, and upon its freedom from adulteration. The following estimations should be made to aid in forming a judgment on these points.

615. Estimation of Water.—Weigh out accurately about 3 grams of the tea in the watch-glasses with clip. Heat this in the steam-oven, until its weight is constant.

616. Estimation of Ash.—Incinerate the dried tea (**615**), little by little, in a weighed platinum capsule or crucible (fig. 47, p. 62), at as low a temperature as possible, and weigh the ash. The total amount of ash thus obtained should not exceed 6 per cent.

Then add water to the ash, and boil. Filter, and wash the residue. Ignite this dry residue, and weigh it.

From these two determinations, the relation between the soluble and the insoluble matter in the ash is calculated. This relation furnishes a valuable indication of the adulteration of tea with spent tea-leaves; since fresh tea-leaves contain a large proportion of soluble mineral matter, which is dissolved out of the leaf during the "mashing." Fresh tea-leaf ash always contains more than 50 per cent. of soluble matter.

617. Estimation of Tannin.—Extract about 10 grams of the tea by boiling it repeatedly with fresh portions of water. Make up the clear extract to 1 litre; and estimate the tannin which it contains, as is described under the assay of sumach (**623**). The amount of tannin usually varies from 12 per cent. in black tea, to 18 per cent. in green tea; but higher proportions occur in tea from certain sources.

618. Estimation of Theine.—The value of tea depends largely upon the amount of theine which it contains. This is estimated as follows.

Extract about 3 grams of the tea with successive small portions of boiling water, allowing ten minutes for each "mashing," and mix these extracts. A Soxhlet extractor (589) may be used for the extraction. Evaporate this liquid nearly to dryness, after adding about half a gram of pure calcined magnesia. Transfer the residual liquid to a small flask; add chloroform, and connect the flask with a reflux-condenser.

Extract for a couple of hours; filter the solution through a dry filter into a tared flask, and wash the residue with a little fresh chloroform. Distil off the chloroform, dry the residue at 100° to 106° C., and weigh the resulting theine. The percentage of theine may vary from 1 to 3 per cent., according to the variety of the tea.

Valuation of Tanning Materials.

619. The exact estimation of tannin in natural tanning materials presents much complication, owing to the fact that there is often present in the same substance a mixture of different tannins. These are also always accompanied by other bodies which, more or less, affect the accuracy of the determination. Probably no process of estimation gives results of scientific accuracy; but two methods which are employed for technical purposes are described below.

One of these methods (621) depends upon causing the tannin from the extract of a known weight of the tanning material to combine with purified hide-powder. The loss of weight of the dissolved material gives the weight of tannin.

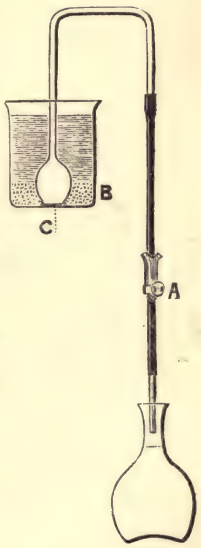
The other method (622), proposed by Löwenthal, estimates the tannin by its deoxidising effect upon standard potassium permanganate solution under suitable conditions.

Of these two methods that depending upon the use of hide-powder is the better one for the tanner, since by its means the amount of tannin concerned in tanning a skin is directly estimated.

620. Preparation of the Extract.—The well "sampled" tanning material (34) must first be suitably broken up and ground, and must then be thoroughly mixed. The soluble matter is now extracted, either by boiling the substance with water and filtering the extract (a), or by the convenient form of combined extraction and filtering apparatus described below (b).

(a). *Extraction by Boiling.*—If the weighed substance is simply boiled with water, it will be found convenient to use about 800 c.c. of water, and to keep this gently boiling with the substance for about three-quarters of an hour. The liquid is then quickly cooled, and transferred completely to a litre-flask; it is made up at once to the mark with water, and thoroughly mixed and filtered. The extraction is sometimes made by successive quantities of water, and is considered complete when the water is no longer coloured.

FIG. 81.



(b). *The Operations of Extraction and Filtration* may be carried out together in the apparatus shown in fig. 81. This represents a beaker (B) as the extracting vessel. A common thistle-funnel (C) has its stem bent twice at right angles, and serves as a siphon to draw off the extract. The mouth of the funnel has muslin tied over it, and is then placed on the bottom of the beaker, and the funnel is held in this position by a clamp. About half an inch layer of sand, which has been purified by treatment with hydrochloric acid, is then poured upon the bottom of the beaker, so as to cover the mouth of the funnel. The prepared tanning material is then poured upon the sand, either in the dry state, or mixed with water in which it has been digested.

As soon as the digestion with water has continued sufficiently long, either at the ordinary temperature or at a higher temperature secured by immersing the beaker in the water-bath, the extract is siphoned over.

This is accomplished by attaching to the shorter arm of the funnel a length of about 30 inches of thin rubber tubing provided with a pinch-clamp (A). The tube is filled by suction and the clear extract is allowed to drop into a flask. The extraction of the tanning material is finished by pouring successive quantities of fresh water into the beaker, and siphoning them over. The process may be considered to be complete when the water is no longer coloured.

The results given by the extract obtained by this method are almost invariably higher than those given by the extract obtained by boiling (a). The best temperature for extraction differs materially with different samples. When this temperature is not known, it is generally best to begin at about 35° C. and then to raise the temperature to 100° as the operation proceeds.

621. The Hide-Powder Process.—The infusion of the tanning material, which is required for this purpose, should contain about 0·6 to 0·8 gram of extract in 100 c.c. In order to obtain an infusion of suitable strength, the following weights of different tanning materials should be extracted by 1 litre of water (620):—

Cutch-cube, gambier, dry extracts, algarobilla, galls,	8 grams.
Block gambier, divi-divi, valonia, myrabolans, mimosa,	10 ,,
Sumach, canaigre, liquid extracts, mangrove bark,	15 ,,
Persea bark, "gambia" pods,	20 ,,
Babool bark, quebracho wood, cork bark,	30 ,,
Oak, hemlock, larch bark,	40–50 ,,

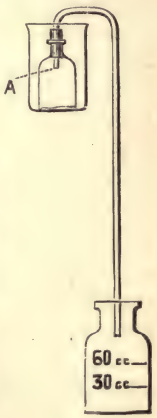
Part of this infusion is reserved, and another part is subjected to filtration through the hide-powder.

Filtration through the Hide-Powder.—The most convenient and efficient form of apparatus for the filtration of the extract through the hide-powder is represented in fig. 82. A bell-shaped vessel (A), about as broad as it is high, may be made by cutting off the upper part of a two-ounce bottle: this

is closed below by muslin, which is held in position by a rubber band round the bottle. About 6 grams of hide-powder are introduced into this vessel. A glass tube is bent twice at right angles to serve as a siphon, the longer limb being about 9 inches in length. The short limb is fitted into the neck of the above vessel by a cork, and its end is closed by a small plug of cotton-wool to exclude the hide-powder.

This filter is placed in a small beaker, into which about 100 c.c. of the extract are then poured in small successive quantities. After about an hour, the siphon is started by suction. About 30 c.c. of the first part of the filtrate, which may contain soluble matter from the hide-powder, are rejected; the rest of the filtrate is retained for the estimation.

FIG. 82.



Estimation of the Solid Matter in the Extract.—It is now necessary to estimate the amount of solid matter present, both in the original extract, and in the extract which has been filtered through the hide-powder.

Fifty c.c. of each of these extracts are measured into two weighed porcelain, aluminium, or nickel dishes, 3 inches in diameter. The extracts are evaporated on the water-bath, and the dishes are weighed, after they have been dried for thirty minutes in the steam-oven and then cooled in the desiccator. A second similar drying process will usually give a constant weight.

From these results the percentage of tanning-matters may be calculated; since the difference in weight shown by the residues from the two extracts compared, represents the weight of soluble tanning-matter.

Thus from four samples of oakwood the following results were obtained:—

Percentage of	A	B	C	D
Total soluble matter, . . .	41·3	35·0	37·8	38·1
Soluble non-tanning matter, . .	14·1	4·7	14·0	4·8
Soluble tanning matter, . . .	27·2	30·3	23·8	33·3

622. The Löwenthal, or Permanganate Method.—This method was originally suggested by Löwenthal: it is now applied in a somewhat modified form. It can only be used for the estimation of the *relative tanning value* of different specimens of *the same tanning material*. It is useless for comparing the relative tanning-value of *different kinds* of tanning materials.

The principles upon which this method depends, are the following.

Solution of potassium permanganate is readily reduced by solution of tannin, and the relative reducing power of some varieties of tannin has been determined. Accordingly if tannin alone could be extracted from the various tanning materials, the amount of it present in the extract could be readily estimated by titration with standard permanganate solution.

But an extract of a tanning material invariably contains other substances besides tannin, which reduce permanganate. Hence it becomes necessary to titrate a portion of the extract with permanganate; and then to titrate a second portion, from which the tannin has been precipitated by means of a solution of gelatin. The difference between the volumes of permanganate solution which are required in the two titrations, represents the volume of permanganate required for the oxidation of the tannin.

In order to limit and make definite the oxidising action of the permanganate on the oxidisable matter, a known volume of indigo-carmine solution is added; and the permanganate solution is added to the extract until the blue colour of the liquid changes to a clear yellow.

The solutions and other chemicals required for the Löwenthal-process are the following.

(a). *Standard Potassium Permanganate Solution.*—One gram of pure permanganate crystals is dissolved in 1 litre of water, and the exact strength of the solution may be ascertained by titration with deci-normal oxalic acid solution, or ammonium oxalate solution (266).

The actual tannin-value of the permanganate solution is then determined by titrating a solution of pure tannin, *under exactly the same conditions as the extract of the tanning material is titrated* (623).

The amount of moisture present in the pure tannin is estimated by drying about 1 gram of it at 100 C.; 2 grams of the tannin are then dissolved in a litre of water, and the solution is used for the titration with the permanganate.

Assuming that the sample of tannin used contains 86·8 per cent. of dry tannin, the 2 grams of tannin will contain $2 \times 0{\cdot}868 \times 1{\cdot}05 = 1{\cdot}8228$ grams of pure dry tannin: and this weight of tannin is contained in 1 litre of the solution. Therefore by means of this standard tannin solution, the tannin value of each c.c. of the permanganate solution can be ascertained.

The factor 1·05 is employed to correct for oxidisable impurities in the tannin.

This process evidently only fixes the tannin-value of the permanganate for estimating the same kind of tannin as that which is used in standardising the solution. A method for extending the titration to other forms of tannin is described in par. 624.

(b). *A Solution of Pure Indigo Carmine.*—This is prepared by dissolving in distilled water 5 grams of pure dry sodium sulphindigotate (Carminum cærul. opt.; Pure Indigotin I, of Gehe & Co.). This solution is filtered, 50 grams of pure sulphuric acid are added, and it is then diluted to 1 litre.

(c). *Dilute Sulphuric Acid* is made by mixing water with one-ninth its volume of the pure strong acid.

(d). *Solution of Gelatin* is made by allowing 2 grams of Nelson's gelatin to soak in 100 c.c. of cold distilled water

for one or two hours, and finally dissolving it by heating the beaker upon the water-bath. This solution should be made only when it is required for use, since it is liable to change; but if 500 c.c. are prepared at once, the addition of 0·5 gram of zinc sulphate will preserve it from alteration for some time, and will not affect the accuracy of the analysis.

(e). *Kaolin*, purified by washing and levigation.

(f). *Sodium Chloride*:—Good table-salt will serve.

623. *The Process of Estimation.*—The estimation of the value of a sample of sumach is made as follows.

An extract of 10 grams of sumach is prepared according to the directions already given (**620**).

Five c.c. of the filtrate are measured into a porcelain evaporating dish 12 inches in diameter, together with 20 or 25 c.c. of the indigo solution (**b**), and 1 litre of distilled water or of good tap-water. The amount of the indigo solution used must be such, that it requires from 14 to 16 c.c. of the permanganate solution to change its colour to pure yellow when it is titrated alone.

The permanganate solution (**a**) is now dropped from a burette, furnished with a glass stopcock, into the mixture in the dish, until the blue colour of the solution begins to change to green. The addition must be made with moderate rapidity, and the liquids must be well mixed by vigorous stirring.

As soon as a green tint appears, the permanganate is dropped in much more slowly, until the solution assumes a dirty greenish-yellow colour. It is best at this stage to allow the liquid to stand for a moment or two, and then to drop in the permanganate, one or two drops at a time, stirring vigorously after each addition. This is continued until the liquid in the dish assumes a clear yellow colour, and shows a faint pink line along its edge. The pink line is only seen in a good light, and is most distinct when the edge of the dish is shaded; it is also best to rest the eyes after each addition of the permanganate, as they rapidly become colour-fatigued.

This titration is repeated more than once; and the results thus obtained should not differ by more than 0·1 c.c. The correspondence of the results is made more certain if the liquid from the first titration of a series is kept, and care is taken that the colour finally obtained in subsequent titrations exactly matches that of the first one. This insures all titrations being carried to the same stage, and although a constant error may be introduced, it will not affect the final result.

The result of this titration corresponds to the total amount of oxidisable matter, both tannin and non-tannin, which is present in the sumach.

50 c.c. of the original filtered solution of the sumach are now introduced into a 100 c.c. stoppered measuring cylinder; 28·6 c.c. of the gelatin solution (d) are added; and the mixture is shaken *very gently* so as to avoid frothing. It is next saturated with common salt, by introducing successive small quantities of that substance in fine powder into the liquid, and gently shaking it until no more is dissolved. This will bring up the volume of the liquid to about 90 c.c. 10 c.c. of the dilute sulphuric acid (c) are then added, and the total volume is made up to 100 c.c. After the liquid has been shaken sufficiently to insure perfect mixture, a teaspoonful of kaolin is added to aid filtration, and the liquid is filtered.

10 c.c. of the filtrate, corresponding to 5 c.c. of the original solution, are then titrated with the permanganate as is described above, two corresponding results at least being obtained. Since the gelatin, in the presence of salt and sulphuric acid, precipitates the tannin-matter; it is evident that the difference between the result of this titration and of the former one, will give the amount of permanganate solution which has been reduced by the tannin-matter itself.

The Following Precautions must be attended to in carrying out the Löwenthal Process.

(1) If the gelatin, kaolin, or salt, which are used to precipitate the tannin, contain any soluble oxidisable impurities, these would render

the titration-result of the non-tannin too high. If very accurate results are desired, it is well to ascertain whether this source of error exists.

This is done by mixing the quantities of indigo solution, distilled water, salt, kaolin, and acid used in a titration ; making this mixture up to 100 c.c. ; then filtering, and titrating the filtrate with permanganate. If the amount of permanganate required exceeds by more than 0·1 c.c. that required by the indigo alone, one-half of this excess must be deducted from the result of the titration of the non-tannin matter, before this is subtracted from the total oxidisable matter.

(2) The indigo solution in this method serves not only as an indicator, but it also controls the oxidising action of the permanganate, by keeping it within certain definite limits. In order to insure a uniform limiting action, the volume of permanganate solution used in a titration must never much exceed one and a half times that required by the indigo alone.

(3) The strength of the extract has an effect upon the accuracy of the determination. It is found that the strength of the tannin solution should not be much below that corresponding to 2 grams of gallotannic acid per litre.

(4) If the titrations are not carried out in a strictly similar manner, as regards stirring and rate of addition of the permanganate, comparable results cannot be obtained ; since the manner of titration considerably affects the ultimate result.

Calculation of the Result from the Tannin Value of the Permanganate (see *Note*).—In a particular estimation, 10 grams of sumach were boiled with water, and the solution was made up to 1 litre and filtered.

5 c.c. of this solution, mixed with 20 c.c. of the indigo solution and with 1 litre of water, were taken for each titration with permanganate, with the following results.

Two titrations required respectively 24·3 and 24·5 c.c. of permanganate solution, the mean result being 24·4 c.c. Therefore 10 c.c. of the sumach solution together with 40 c.c. of indigo solution, would require 48·8 c.c. of permanganate.

After the addition of gelatin, salt, and acid, 10 c.c. (equal to 5 c.c. of original solution) required as a mean 19·3 c.c. of permanganate. Therefore 10 c.c. of the original solution, deprived of tannin, together with 40 c.c. of indigo solution, would require 38·6 c.c. of permanganate solution.

Accordingly, $48{\cdot}8 - 38{\cdot}6 = 10{\cdot}2$ c.c. of permanganate were reduced by the tannin contained in 10 c.c. of the original solution.

Therefore 1 litre of that solution would require $10{\cdot}2 \times 100 = 1020$ c.c. But the litre of solution contained the extract from 10 grams of

sumach. Therefore the tannin in 100 grams of the sumach would require $1020 \times 10 = 10200$ c.c. of permanganate solution.

The standard tannin solution contained 1·8228 grams of pure tannin per litre (**622, a**). 5 c.c. of this solution, with 20 c.c. of the indigo solution, required 23·5 c.c. of the permanganate. Therefore 10 c.c. of the standard solution, with 40 c.c. of the indigo, would require 47 c.c. of the permanganate.

But 40 c.c. of the indigo solution require 34 c.c. of the permanganate. Therefore 10 c.c. of standard tannin solution require $(47-34) = 13$ c.c. of the permanganate. Hence each c.c. of the permanganate corresponds to $\left(\frac{1{\cdot}8228}{1000} \times 10\right) \div 13 = 0{\cdot}001402$ gram of pure tannin. Consequently the percentage of tannin in the sumach $= 10200 \times 0{\cdot}001402 = 14{\cdot}3$.

Note.—Results were formerly calculated directly from the oxalic acid value of the permanganate ; but it has been found that although this value is comparatively constant in the hands of any one experimenter who adheres to a uniform method of titration, yet it differs so widely with slight differences in stirring and in the rate of addition of the permanganate, that the results are quite useless for comparison.

This is due to the large amount of secondary oxidation which takes place when the indigo becomes nearly exhausted.

This source of error is almost entirely avoided by standardising the permanganate with pure tannin as is directed above (**a**), since the amount of secondary oxidation is then practically the same in the titration of the pure tannin as in the titration of the extract.

624. Determination of the Absolute Percentage Weight of any Form of Tannin.—If it is desired to determine the *actual* percentage weight of any other form of tannin besides gallotannic acid in a sample of tanning material by the Löwenthal method, it is necessary to resort to the gravimetric process already described (**621**) in order to standardise the permanganate solution.

A portion of the original infusion (**620**) is titrated as is directed above (**623**). A portion of the same infusion is also passed through the hide-powder filter (**621**), and is then similarly titrated in order to estimate the amount of non-tannin matter present. 50 c.c. of the original infusion and 50 c.c. of the filtrate from the hide-powder are then evaporated separately, and the residues are dried for thirty minutes in the steam-oven and weighed. The actual weight of the tannin matter, which corresponds to the permanganate reduced, can then be calculated.

This method is obviously useless for a single estimation ; but when a number of titrations of similar tanning infusions are being made, it is often very convenient. In some cases the proportion of non-tannin matter can be assumed to be constant, and the strength of an infusion is then obtained by a single titration.

Soap Analysis.

625. In an ordinary analysis of soap, it is not necessary to estimate all the constituents. The following determinations will commonly suffice:—water, free and combined alkali, fatty acids, and insoluble matter.

A more complete chemical examination of the soap would include the estimation of the amount of free fat, of resin, of glycerine, and of certain other substances. In many cases also an investigation is required into the nature of the fatty acids present.

Two schemes of analysis are drawn out below, a scheme for partial analysis (**626–631**), and a scheme for more complete analysis (**626, 632**).

626. Preparation of an Average Sample for Analysis.—The following special method of preparing an average sample for analysis should be adopted, since soap contains a large proportion of water, which is differently distributed throughout its mass, the outside of the sample usually containing much less moisture than the inside.

Cut out a slice of the soap quite through the middle of the bar, and at right angles to its long axis. This slice must weigh exactly 50 grams, or else the volume to which the soap solution is diluted must be adjusted accordingly. Warm the soap with air-free distilled water until it is dissolved. Then dilute the solution, and filter it if necessary through a dried tared filter.

The Insoluble Matter is dried and weighed.

The warm solution is cooled in a 500 c.c. flask to about 60° C., below which temperature it is apt to gelatinise. It is then made up to the mark with air-free water at 60° C.; and the liquid is thoroughly though gently mixed by inverting the flask. If the liquid is violently agitated it will froth seriously. Several portions of 50 c.c. and 100 c.c. each are then at once measured off by heated measuring-flasks into separate vessels for analysis.

An alternative method is to make the solution up to a

500° C. at 60° C., and to bring it to the liquid state in the stoppered measuring-flask, when necessary, by warming the contents of the flask to 60° C. The soap-solution must always be thoroughly mixed, if it has been allowed to stand aside before measuring off portions for analysis.

627. Estimation of Moisture.—Evaporate 50 c.c. of the above solution of the soap to dryness in a weighed platinum or porcelain dish upon the water-bath. Dry the soap-residue in the steam-oven, or in an air-bath at 120° C., until the weight is constant. Subtract the weight of the residue from 5, to obtain the weight of water in 5 grams of the soap.

628. Estimation of Matter Insoluble in Alcohol.—Transfer the dried soap from the dish (627) as completely as possible to a 6-inch filter. This filter must have been previously treated with alcohol, and dried at 100° until it is of constant weight. The amount of soap which is thus removed to the filter is found by reweighing the dish. The filter should be pressed round the soap, so as to enclose it in a bag.

Place the filter containing the soap in the Soxhlet-extractor (589). Pour absolute alcohol into the flask; drop in a few pieces of platinum-foil to prevent the alcoholic solution of soap from bumping; then boil the spirit, and allow the extraction to continue for two hours.

The filter will now contain any matter insoluble in alcohol, which was present in the soap, such as starch, silica, and alkaline carbonate. Dry the filter with its contents in the steam-oven until its weight is constant.

The amount of mineral matter in this residue may then be obtained by incinerating the residue and filter at the lowest temperature possible.

629. Estimation of the Alkali present as Hydrate, Carbonate, and Silicate.—Since evaporation of the soap-solution would convert free alkali into carbonate, it is neces-

sary to dissolve a slice of the soap (626), weighing 20 grams, in 200 c.c. of absolute alcohol. This solution is filtered, and 50 c.c. of the filtrate are titrated with normal sulphuric acid, using phenol-phthalein as an indicator. This titration gives the amount of *sodium hydrate* present (see *Note*).

The residue on the filter is dissolved in water, and the solution is titrated with standard acid and methyl-orange, to estimate the amount of Na_2O present as *carbonate and silicate.*

Note.—The above separation of sodium hydrate from sodium carbonate by means of absolute alcohol is frequently not complete. If the alcohol is quite absolute some NaOH remains undissolved, while if water is present some Na_2CO_3 may pass into solution.

630. Estimation of the Fatty Acids.—The fatty acids in the soap may be determined in the alcoholic solution (629), which has been neutralised with the normal acid as is described above. If this course is adopted, the solution must be diluted with water, and then boiled until all the alcohol is removed.

Or 50 c.c. of the original soap-solution (626) may be used for the determination.

In either case, add a measured quantity in excess of normal sulphuric acid to the soap-solution contained in a beaker, a dish, or a conical flask. Heat the vessel on the water-bath, until the fatty acids form a thin layer on the top of the liquid, leaving a clear solution below.

The fatty acids are most conveniently separated from the liquid in a dish and washed, by using the "butter-flask" as is directed in paragraph 600. The weight of fatty acids found is multiplied by 0·97, in order to obtain the weight of the fatty anhydrides.

Another method is to decompose the soap-solution by the acid in a conical flask or in a beaker. This is cooled until the fatty acids set into a solid cake. The aqueous solution is filtered through a wetted filter. The fatty acids in the flask are washed by shaking them with hot water, cooling, and pouring off the aqueous portion again (see *Note*). This washing process is repeated until the washing-water no

longer affects blue litmus-paper. If the washing is carefully performed, very little fatty acid will be present on the filter.

The funnel, containing the filter, is placed in a small beaker and dried in the steam-oven. The fatty acids are dissolved from the filter by means of alcohol, and the solution is added to the fatty acids in the flask. The flask with its contents are then heated in the steam-oven, until its weight is constant. The weight of fatty acids thus found is multiplied by 0·97, in order to obtain the weight of the fatty anhydrides.

Note.—Instead of washing the fatty acids upon the filter, they may be removed as a cake, which is washed with cold water. For this purpose 5 grams of white wax are weighed out, and are melted with the fatty acids in the beaker on the water-bath after the normal acid has been added. On cooling the flask a firm cake is obtained, which can be rinsed with cold water, drained, dried with filter-paper, and weighed. From this weight the weight of the wax is then subtracted.

631. Estimation of the Total Alkali.—All the alkali will be contained in the aqueous filtrate (630), if the original soap-solution was employed for the estimation of the fatty acids. If, however, the alcoholic solution (629) was used for the estimation of the fatty acids, the aqueous filtrate (630) will contain the total alkali, less that present in the insoluble residue (629).

The amount of alkali present in the aqueous filtrate (631), in either case, is obtained by titrating the liquid with standard sodium hydrate solution, when the excess of standard acid will be obtained. From this the quantity of acid corresponding to the total alkali in the soap, and the amount of combined alkali (Na_2O) can be calculated.

632. Potash soap or Soft soap.—Since the alkali present in this soap is potassium oxide, the alkali must be calculated as K_2O instead of as Na_2O. If both sodium and potassium are to be estimated, a measured volume of the soap-solution (626) is decomposed by hydrochloric acid (630), and the alkali-metals are determined in the filtrate from the fatty acids according to pars. 358, 359.

633. Complete Analysis of Soap

Measure 50 c.c. of the Soap-Solution (626), evaporate this on the water-bath, and dry
Weight of Water in 5

Remove this Residue to a tared filter, which has been extracted with petroleum ether, and treat

Ether Extract. Distil off the ether, and dry the flask at 100° C., until its weight is constant. The residue is **Uncombined Fat.**

Note. — Essential oils and certain adulterants may be present in this residue.

The Residue in the filter consists of soap and other

The Alcoholic Extract contains soap (fatty anhydride and combined alkalis), resin, and glycerine. Add a few drops of phenol-phthalein, and exactly neutralise with dilute H_2SO_4 if free alkali is shown to be present by the colour of the phenol-phthalein.

Free Alkali. For this estimation refer to par. **629.**

Add a large excess of water, and boil off all the alcohol. Decompose the soap by adding a measured volume in excess of normal H_2SO_4; boil, separate the free fatty acids (**630**), filter, and wash.

The Filtrate contains combined alkali and glycerine. Titrate it with normal sodium hydrate solution.

From the volume of sodium hydrate solution used, the H_2SO_4, which corresponds to the **Combined Alkali**, is known.

The amount of the combined alkali is calculated as Na_2O.

After titration, evaporate the liquid to dryness on the water-bath. Heat the residue with 1 part of chloroform and 2 parts of absolute alcohol; evaporate the clear alcoholic solution to dryness in a tared dish; and weigh the residual **Glycerine.**

Note. — The residue should be incinerated, and the weight of any ash thus found must be deducted from that of the glycerine.

The Residue on the filter-paper consists of **Fatty Acids and Resin.** Dry it at 110° C., and weigh.

Dissolve an aliquot part in 20 c.c. of strong alcohol; saponify by heating with sodium hydrate solution added in slight excess, using phenol-phthalein to ascertain when excess is present. Boil, cool, transfer to a stoppered cylinder, and add ether until the volume is 100 c.c. Add a fair quantity of $AgNO_3$ in fine powder, shake well for ten minutes, and allow to settle.

The Precipitate, which consists of stearate, palmitate, and oleate of silver, is rejected.

The Solution consists of resinate of silver. Filter off 50 c.c. from the total 100 c.c. Decompose this with 20 c.c. dilute HCl (1 of acid : 2 of water). Allow the AgCl to settle, and evaporate the 50 c.c. of ethereal solution in a tared dish. Dry at 110° C., and weigh **The Resin.** For each 10 c.c. of solution evaporated, subtract 0·00236 gram, to correct for dissolved oleic acid; this is a rough correction only.

Subtract double this corrected weight from the corresponding weight of the fatty acids + resin. The weight of the fatty acids thus obtained is then multiplied by 0·97 (**630**).

(Modification of Leed's Scheme).

the residue at 100° C. The weight of this residue, when subtracted from 5, gives the grams of the soap.

the residue, wrapped up in the filter-paper bag, with petroleum ether in the Soxhlet-apparatus (589).

constituents. Treat this with alcohol in the Soxhlet-apparatus.

The Residue consists of Na_2CO_3, NaCl, Na_2SO_4, sodium silicate, starch, and insoluble matter. Wash with 60 c.c. of cold water.

The Filtrate consists of Na_2CO_3, NaCl, Na_2SO_4, and sodium silicate. Make the solution up to 100 c.c., and use separate portions of 20 c.c. each for the following estimations.

The Residue consists of starch and insoluble matter. Dry at 100° C., and weigh the **Starch+Insoluble Matter.**

Na_2CO_3. Titrate with normal H_2SO_4, and calculate the result as **Na_2CO_3.** This will include any Na_2O originally present as silicate and as hydrate (629).

NaCl. Titrate with $AgNO_3$ (304); or precipitate as AgCl, and weigh (113). Calculate the result as **NaCl.**

Na_2SO_4. Acidify with HCl, precipitate with $BaCl_2$ solution, and weigh the $BaSO_4$ (96). Calculate as **Na_2SO_4**

SiO_2. Decompose with HCl, evaporate down to dryness, and determine the Silica in the residue (172).

Boil the residue with about 100 c.c. of water. Place the solution in a small bottle, and add 1 c.c. of strong H_2SO_4. Cork the bottle, and wire down the cork tightly. Heat the bottle and its contents on the water-bath for several hours. Then neutralise the excess of acid, titrate the glucose thus formed by Fehling-solution (612), and calculate the weight of the **Starch.**

The weight of the **Insoluble Matter** is found by difference.

SECTION IV.

ORGANIC ANALYSIS.

640. Introductory Remarks.—This Section treats of the general and typical methods employed for the ultimate analysis of organic substances, and for the determination of their molecular weights.

Carbon and hydrogen, the most common constituents of an organic compound, are estimated by burning a known weight of the organic substance, and determining separately the weights of carbon dioxide and of water which are thus produced. There is no simple method for directly determining with accuracy the proportion of oxygen present: oxygen is usually calculated by difference, after all the other constituents have been determined.

Several methods for determining nitrogen are described. The estimation is an important one, not only for scientific purposes, but also in connection with the analysis of manures and agricultural products.

The halogen elements, as well as sulphur and phosphorus, occasionally require to be determined, mainly for scientific purposes. Methods of determining them are therefore described.

A large number of other elements are now known to exist in organic compounds. As a rule methods of estimation, which are described in the earlier part of this book, are directly or indirectly applicable to their determination.

Estimation of Carbon and Hydrogen in a Solid Organic Substance.

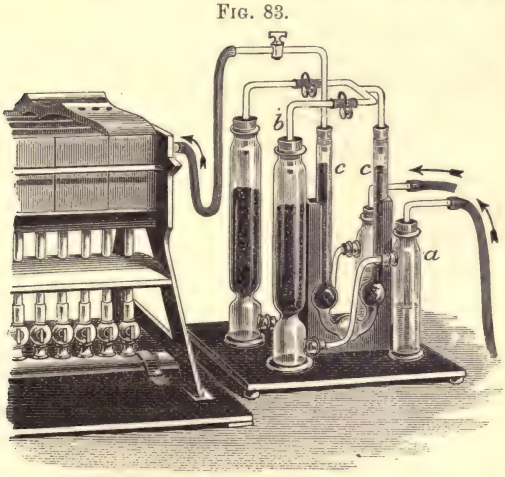
641. Organic Combustion Process.—The method pursued is a modification of that first described by Liebig. It consists in heating the organic substance to redness with copper oxide, whereby its hydrogen is converted into water, and its carbon into carbon dioxide. These products are absorbed by calcium chloride, and by soda-lime or potassium hydrate solution, respectively.

In the method now commonly in use, the "combustion" of the organic substance, and the removal of the products, are assisted by passing a current of air or of oxygen through the combustion-tube.

The following apparatus and materials are required for an organic combustion.

642. Apparatus for Purifying the Air and Oxygen used in the Combustion.—This apparatus (fig. 83) is in duplicate,

Fig. 83.



with the exception of the U-tube (*c*). The front wash-bottle (*a*), and the eprouvette (*b*), are used for purifying air;

and the corresponding vessels behind them are used for purifying oxygen. The wash-bottles (*a*) are connected respectively with supplies of air and of oxygen under pressure.

Either air or oxygen, or both, may therefore be passed in a purified condition into the combustion-tube, by suitably adjusting the clamps between the eprouvettes and the U-tube (*c c*).

Both the air and the oxygen finally pass through the U-tube (*c*) on their way to the combustion-tube. The air is usually passed from a gas-holder; the oxygen may be supplied either from a gas-holder or from a steel cylinder charged with the compressed gas.

The two wash-bottles (*a*) contain strong sulphuric acid, and serve to dry the gas passing through them; at the same time they give an indication of the speed of the current of gas. The eprouvettes (*b*) contain granular soda-lime, which absorbs the carbon dioxide. Any moisture which is taken up by the gas from the soda-lime, is subsequently removed during the passage of the gas through the calcium chloride in the U-tube (*c*).

Fit up the apparatus as is shown in fig. 83, using either rubber stoppers, or good corks which are cut off level with the tube after being fitted in, and are then brushed over with melted paraffin-wax. The wash-bottles (*a*) are one-third filled with pure strong sulphuric acid.

The lower chambers of the eprouvettes (*b*) contain broken glass, and the bodies of these vessels are charged with granular soda-lime. The U-tube (*c*) is filled with granular calcium chloride, a plug of glass-wool being inserted in the top of each limb.

643. A Combustion Furnace.—Of the many forms of gas combustion-furnace, Erlenmeyer's, fig. 87 (p. 410), will perhaps be found the most convenient. Part of the Gläser furnace is shown in fig. 83 (p. 391). A sheet-iron trough, lined with a thin layer of asbestos, should extend down the whole length of the furnace. The combustion-tube is laid in this trough.

644. The Combustion Tube.—Cut off a piece of combustion tubing, about five-eighths of an inch in internal diameter, to a length of about 30 inches. Round off the sharp edges at each end by fusing them in the blowpipe-flame. As soon as the glass is cold, cleanse the interior by washing it with a long-stemmed tube-brush in a stream of water; or by attaching a plug of cotton-wool to the middle of a piece of string about 5 feet in length, and drawing the wetted plug up and down the tube, afterwards rinsing the tube well in a stream of water from the tap.

645. A Glass Plug to prevent Diffusion is shown at *d* in fig. 84 (p. 395). This is made by drawing off about an inch of a glass tube or rod, which just passes into the combustion-tube. The narrow portion is cut off about half an inch from the shoulder, and the end is bent round into the form of a loop, or a loop of platinum wire is fused into the end. This loop enables the plug to be withdrawn from the combustion-tube by means of a piece of hooked wire.

646. A Platinum or Porcelain Boat is shown at *e* (fig. 84). Select a boat of such dimensions, that it can be readily pushed into the combustion tube. The boat may be made from platinum-foil.

647. Copper Oxide.—Granular copper oxide, which has been prepared by the direct oxidation of metallic copper, must be procured. The oxide is usually prepared by roasting short lengths of copper wire in a current of air.

If the oxide has been prepared by the ignition of copper nitrate, it often evolves oxides of nitrogen when it is heated, and is unsuitable.

648. A Silver or Copper Coil.—A strip of silver-sheet or gauze, about 2 inches in width, is tightly coiled until it will just pass into the combustion-tube (fig. 84, *g*).

A similar coil of copper-gauze may be used in certain cases instead of the silver one.

The object of the copper or silver coil is to deoxidise any oxides of nitrogen which may be evolved from a nitrogenous organic substance, and to prevent these oxides from being absorbed by the soda-lime, and weighed as carbon dioxide.

The *silver coil* has the further advantage of absorbing halogens.

649. Calcium Chloride Absorption Tube.—The tube *h* (fig. 84), which is intended to absorb the aqueous vapour evolved during the combustion, contains granular calcium chloride (**142**), through which CO_2 has been passed until it is neutral.

The bulb nearest to the combustion-tube is empty (see *Note*).

The other bulb and the two limbs of the U-tube are nearly filled with the calcium chloride, after a small plug of glass-wool has been placed at the top of the second bulb, to prevent the calcium chloride from passing into the narrow tube above.

Another plug of glass-wool is then placed in the other limb of the tube, to prevent particles of calcium chloride from entering the small side-tube. The straight limb is closed with a well-fitting cork, which is cut off level with the top of the tube, and is then brushed over with melted paraffin-wax.

Note.—The greater part of the water which is produced during the combustion collects in the empty bulb, and is emptied out after each combustion. The calcium chloride tube is thus made to serve for several determinations.

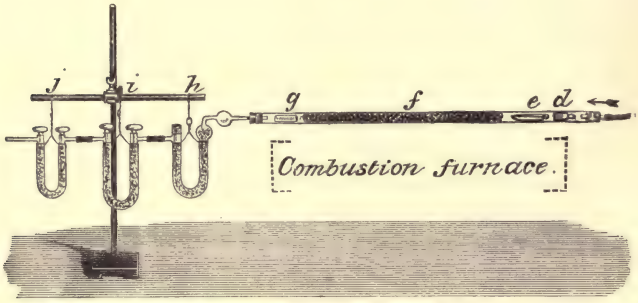
650. Soda-lime Tubes.—These tubes (*i*, *j*, fig. 84) are intended to absorb the carbon dioxide which is formed during the combustion. Each tube is filled to three-quarters of its capacity with granular soda-lime, the remainder of the tube being filled with granular calcium chloride. Each side-tube is protected by a plug of glass-wool. The description of the preparation of similar tubes in paragraphs **142**, **143** should be consulted.

All tubes and vessels containing absorbent material must be closed from the air, when they are not in actual use.

Potash Bulbs.—Potassium hydrate solution may be used instead of soda-lime as an absorbent for the carbon dioxide. It is contained in a multiple bulb-apparatus. Either Liebig's or Geissler's potash-bulbs serve well. The liquid presents the advantage of serving as a gauge to indicate the rate at which the process of combustion is proceeding by the speed of passage of the bubbles. A guard-tube containing fragments of solid calcium chloride must be attached to the further end of the bulb-apparatus, and must be weighed with it. This tube serves to prevent moisture from being carried away from the apparatus during the combustion.

651. The Combustion Apparatus is fitted up as follows.—Fill about two-thirds of the combustion-tube (**644**) with granular copper oxide (**647**), compactly shaken together

FIG. 84.



(*f*, fig. 84). The oxide is kept in its place by means of coiled cylinders of copper-gauze placed before and behind it. Each of these cylinders is made by tightly coiling a strip of copper-gauze; it is about 1 inch in length, and of such diameter that it just passes into the combustion-tube.

Now lay the tube on the asbestos in the iron trough of the combustion-furnace, with its ends projecting about an inch and a half from the furnace. Push upon the ends of the tube perforated discs of sheet-iron or of asbestos millboard to protect the corks from the heat of the furnace.

The silver-roll (**648**) is then introduced (*g*), sufficient room being left in the tube for the insertion of the boat (*e*), and for the diffusion-plug (*d*).

Two sound dry corks are now selected to fit the ends of the combustion-tube. One cork is perforated for a small glass tube; it is then inserted into the empty end of the combustion-tube, and is connected by means of rubber tubing with the purifying apparatus (642).

The other cork is perforated to admit the bulbed-tube (*h*) at the end of the calcium chloride tube (649); this tube is inserted so as to project through the cork about one-eighth of an inch. The cork is then pushed into the other end of the combustion-tube.

The soda-lime tubes (*i*, *j*) are then connected in succession with one another, and with the calcium chloride tube, by means of rubber joints, the soda-lime in each of these tubes being in the limb which is nearer to the tube (*h*). The glass tubes are made to touch one another within the rubber-joints, and are bound with copper binding-wire if the joints are not air-tight.

652. **Now proceed to Heat the Combustion-Tube,** containing the copper oxide and the silver cylinder, to redness for at least half an hour with a current of purified air passing through it, so as to remove all combustible matter and moisture.

Before the heating of the tube is stopped, it is best to ascertain that its contents are no longer evolving carbon dioxide or steam, by attaching the weighed absorption-tubes (*h*, *i*, *j*) for half an hour. These tubes are then reweighed, and should have undergone no increase in weight.

For this purpose weigh the tube (*h*) without its rubber caps or connections. As soon as the weighing is finished, slip a little piece of rubber tube closed with a piece of glass rod, upon each of its ends, so as to prevent access of atmospheric air. The tubes (*i*) and (*j*) are then weighed separately, and are immediately closed with similar caps, unless they are so constructed that by turning their stoppers contact with the air can be prevented (143).

Now connect these tubes with one another, and with the

combustion-tube, as is shown in fig. 84. Then regulate the speed of the current of air passing through the apparatus, until the bubbles follow one another through the sulphuric acid (*a*, fig. 83, p. 391) at such a rate that they can be easily counted.

Remove the absorption-tubes after they have been in connection with the combustion-tube for half an hour, and again weigh them. If any one of them is found to have increased in weight more than a few milligrams, the above test must be repeated.

It will be understood that the above process of preparing and testing the combustion-tube and copper oxide need only be applied when a new combustion-tube and its contents are used, or when the tube has been laid aside for some time. A series of combustions may succeed one another ordinarily without any such testing being necessary.

653. For Practice in the Combustion Process, weigh out accurately into the boat about 0·25 gram of pure crystallised cane-sugar, which has been recently dried in the steam-oven. Now connect the parts of the apparatus together (**651**); push in the boat with the sugar, and the diffusion-tube; and ascertain that the whole is air-tight (**144**).

The presence of the silver or copper coil (*g*) in the combustion-tube during this combustion is unnecessary, since sugar contains no nitrogen; but the coil need not be withdrawn.

Now heat the whole of the copper oxide (*f*) to redness, protecting the boat from radiated heat by a small screen. Then start a slow current of air through the tube, the bubbles passing at such a rate that they can be easily counted. Extend the heating to the boat *very gradually*, so as to avoid a rapid evolution of gas and vapour from the sugar. The sugar will be slowly burnt away.

In burning some substances, an oxygen current should replace the air at the last, to burn off traces of carbon; but this is not necessary in the case of sugar.

As soon as the whole of the sugar is burnt, the current of air is allowed to pass slowly for fifteen minutes, in order to sweep out the carbon dioxide and steam from the combustion-tube, and to reoxidise the metallic copper formed by the reduction of the copper oxide.

If any water condenses in the end (*g*) of the combustion-tube, it may usually be removed by shifting the screen on the end of the combustion-tube, so as to allow the tube to become gently heated while the air-current is passing. The water must be all transferred to the calcium chloride tube in this way.

The absorption-tubes may then be detached from the combustion-tube and from one another, their contents being at once shut off from contact with the atmosphere. After they have stood for half an hour, so as to gain the temperature of the air, each tube is weighed separately.

The increase of weight of the calcium chloride tube (*h*) gives the weight of water produced by the combustion of the sugar; from this the weight of hydrogen in the sugar can be calculated. The combined increases of weight of the soda-lime tubes (*i*, *j*) give the amount of carbon dioxide, produced by the combustion of the sugar; from this the weight of carbon in the sugar can be calculated.

The smaller soda-lime tube (*j*) serves as a "guard-tube." If its weight increases during the combustion, either the soda-lime in the first tube (*i*) is not absorbing carbon dioxide satisfactorily, and requires to be replaced by fresh; or the combustion has been carried on too rapidly, and in that case the guard-tube serves to prevent the loss of carbon dioxide, which has passed through the first soda-lime tube.

The Method of Calculating the Results obtained in an organic combustion is shown below.

Example.—In a particular combustion, 0·4739 gram of pure sugar was burnt.

The calcium chloride tube, which weighed 48·769 grams before absorption, gained 0·2727 gram in weight by absorbing the water formed during the combustion.

The soda-lime tube, which weighed 58·4891 grams before absorption, gained 0·728 gram in weight.

Therefore the weight of hydrogen in the sugar $= \frac{0{\cdot}2727}{9} = 0{\cdot}0303$ gram.

And the weight of carbon in the sugar $= \frac{0{\cdot}728 \times 3}{11} = 0{\cdot}1985$.

Therefore the percentage weight of hydrogen is $\frac{0{\cdot}0303 \times 100}{0{\cdot}4739} = 6{\cdot}39$.

And the percentage weight of carbon is $\frac{0{\cdot}1985 \times 100}{0{\cdot}4739} = 41{\cdot}88$.

Estimating the weight of oxygen by difference, and comparing the results with those calculated from the formula for cane-sugar, $C_{12}H_{22}O_{11}$, the following statement is the result:—

	Theoretical.	Found.	Error.
Carbon, . .	42·10	41·89	−0·21
Hydrogen, .	6·43	6·39	−0·04
Oxygen, . .	51·47	51·72	+0·25

Any Incombustible Mineral Matter which is present in an organic substance will remain as ash in the boat. Its weight may be determined by weighing the boat and ash, and then the empty boat.

The Presence of Nitrogen in the organic substance leads to danger of nitrogen oxides escaping with the products of the combustion. These oxides might be taken up by the absorption-tubes, and would then lead to error.

To prevent this, the coil of silver or copper (648) is introduced into the front of the combustion-tube, and is kept at a red heat during the combustion. The nitrogen oxides are thus decomposed into oxygen and nitrogen, and are prevented from being absorbed.

A more satisfactory method is to absorb the nitrogen oxides by the following mixture:—A strong solution of K_2CrO_4 with one-tenth its weight of $K_2Cr_2O_7$, is made into a thick paste with precipitated manganic hydrate, and the mixture is heated until it is dry. About 5 inches of this granulated substance is then placed in the front of the combustion-tube, and is always heated to redness while the preliminary current of air passes through the tube. It is allowed to assume a temperature of about 200° C. during the combustion.

The Halogen Elements, if present in an organic substance, are also evolved during its combustion in a condition in which they may remain in the absorption-tubes. They may be completely absorbed in the combustion-tube itself by causing them to pass over the red-hot silver coil. The copper coil is useless for this purpose.

654. A Volatile Solid Organic Substance requires to be burnt much more carefully than a non-volatile body like sugar. The substance must only be introduced into the rear of the combustion-tube after the front part of the tube has been heated to redness. The substance must then be very slowly heated.

In order to assist the diffusion-plug (**645**) in preventing the passage of the vapour backwards against the direction of the air-current, a "mercury valve" may be inserted between the combustion-tube and the purifying apparatus (fig. 84, p. 395). The valve consists of a small test-tube, which is fitted with a doubly-perforated cork, and contains half an inch of mercury.

Through one perforation a bent tube passes, which just dips beneath the mercury, and is connected at its end with the purifying apparatus: through the other perforation a shorter bent tube passes, which is in connection with the combustion-tube, and contains a plug of cotton-wool to prevent mercury from passing over. This valve checks the passage of any gas or vapour out of the combustion-tube towards the purifying apparatus.

Combustion of a Liquid Substance or Gas.

655. A Liquid Organic Substance, if it is neither very volatile nor very hygroscopic, may be weighed in the boat and burnt in the usual way.

656. A Volatile Organic Liquid is weighed in a little bulb-tube, and the bulb is introduced into the combustion-tube.

This bulb-tube is made by drawing out a short piece of glass quill-tubing into capillary-bore in two parts about a quarter of an inch

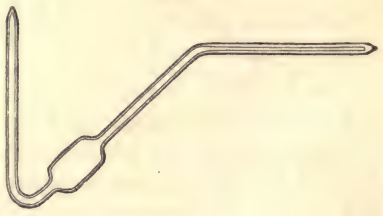
apart. One of the capillaries is then drawn off close to the short piece of tube, so as to seal it. The little piece of quill-tube between the narrowed parts is then heated to redness in the flame, and is expanded into a bulb by blowing down the other capillary-tube. While the tube is being heated it should be constantly rotated. The capillary-tube is then broken off at a distance of about an inch and a quarter from the bulb.

The empty bulb-tube is first weighed. The liquid is then introduced into it in suitable quantity, by heating the bulb, and allowing it to cool with the end of the capillary immersed in the liquid. The end of the capillary-tube is then sealed in the flame, and the bulb is weighed again. Its gain in weight will give the weight of liquid taken.

A slight scratch with a file is made near the end of the capillary, in order that it may be easily broken off. The end is broken off and is placed together with the bulb in the boat, just before the boat is pushed into the combustion-tube.

657. A Very Volatile Substance should be heated in a tube *outside* the combustion-furnace. A convenient form of tube is shown in fig. 85. The liquid is weighed in this tube, which is readily made from a piece of ordinary glass tube, and both ends are sealed up before weighing. The tube is then placed either in a dish of cold water, or in ice and salt, according to the degree of volatility of the liquid.

FIG. 85.



When the combustion-tube has been heated to redness, the horizontal end of the bent tube is opened, and is at once pushed through a hole in the cork of the combustion-tube, into which it must fit tightly. The temperature of the liquid is then allowed to rise, when the vapour will be *gradually* evolved and burnt. As soon as the liquid has volatilised, the upright end of the tube is

snapped off, and air or oxygen is passed through the tube, as has been already described (653).

658. **Gaseous Organic Substances** are burnt by passing them in known volume through the combustion apparatus which has been described for solids and liquids (651).

ESTIMATION OF NITROGEN IN AN ORGANIC SUBSTANCE.

659. Three methods for the estimation of nitrogen in an organic substance are described below.

The method of burning with soda-lime and estimation of the ammonia evolved (660) is the one usually adopted when practicable.

The second method (663) is rapid, and is frequently used for the estimation of nitrogen in organic products, such as manures and vegetable products, or in cases where the body is in a liquid or a moist condition.

The third method (664) is applicable to all nitrogenous substances.

ESTIMATION OF NITROGEN BY THE SODA-LIME METHOD.

660. This process is not adapted to the combustion of nitro-compounds, and of certain other bodies.

The substance is mixed with soda-lime, and the mixture is heated to dull redness. The nitrogen in the organic body is thus converted into ammonia gas. The ammonia which is evolved may be estimated in the two following ways, of which the latter is the more exact but the more tedious process.

(1) It may be absorbed in a known volume of standard acid, the amount of free acid being afterwards determined by standard sodium hydrate solution (661).

(2) The ammonia may be absorbed in excess of dilute

hydrochloric acid, the ammonium chloride thus produced being then precipitated as the double chloride of ammonium and platinum, and weighed as such (662).

661. The Ammonia is absorbed in an excess of Standard Acid, and is Estimated Volumetrically.

The following materials are required for the process.

(a). *A Combustion-tube* about 18 inches long and five-eighths of an inch in internal diameter, which has been closed at one end and rounded off in the flame at the other end.

(b). *A Will-and-Varrentrapp Bulb-tube*, which is fitted into the open end of the combustion-tube by means of a tightly-fitting perforated cork (fig. 86). The end of the bulb-tube projects about one-eighth of an inch through the cork.

(c). *Soda-lime* in the state of fine powder, and in a granular condition (142). This must be heated in a dish over a sand-bath so as to be perfectly freed from moisture and from ammonia; and the powder and granular substance should then be kept in separate well-stoppered bottles.

(d). *Fibrous Asbestos*, which has been ignited in a porcelain or platinum crucible.

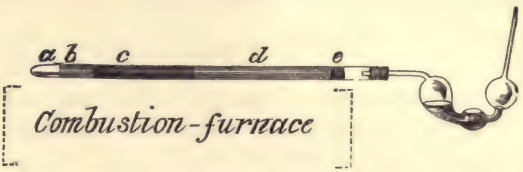
(e). *Oxalic Acid*, which has been heated in the steam-oven, until all its water of crystallisation has been expelled.

(f). *For Practice in the Process*, weigh out carefully about 0·3 gram of pure dry urea, CON_2H_4. Hold the perfectly clean and dry combustion-tube in a vertical position, with its closed end resting on a square of glazed paper. Introduce into the tube a layer, about 1 inch in depth (fig. 86, *a*), of the dried oxalic acid. Next add $1\frac{1}{2}$ inches of the dry powdered soda-lime (*b*).

Turn out the weighed quantity of urea into a clean, dry, porcelain mortar, and add finely-powdered soda-lime in suffi-

cient quantity to make the mixture occupy about 4 inches of the tube. Gently, but thoroughly, mix the urea and soda-lime in the mortar, and then pour the mixture into the tube through a funnel made of glazed paper. When all the

Fig. 86.



mixture has been introduced, rinse out the mortar with a little fresh soda-lime powder, and pour this also into the tube. The mixture and rinsings should fill the part of the tube shown by special shading (*c*).

Now fill in about 9 inches of the granular soda-lime (*d*), and finally push in a loose plug of the ignited asbestos (*e*).

After the introduction of the asbestos, about three-quarters of an inch of the tube should remain clear. Tap the whole length of the tube, held in a horizontal position, upon the bench, to make sure that there is a free passage along the upper part of the tube for the evolved gases.

Note.—If the substance to be burnt is hygroscopic or volatile, it should be mixed with the powdered soda-lime in the combustion-tube instead of in the mortar. For this purpose a long wire, shaped like a cork-screw at its end, is used.

Now measure out 15 c.c. of normal sulphuric acid (**236**) into the bulb-tube, by means of a fine pipette. Add a little water to make up the liquid to the level shown in the figure. Connect the bulb-tube with the combustion-tube by means of the cork, and make sure that the joint is gas-tight.

The tube is now ready for the combustion. Lay it upon the asbestos in the trough of a combustion-furnace, with the end (*e*) extending about an inch beyond the end of the furnace. Slip upon this end of the tube a circular piece of sheet-iron or asbestos cardboard about 3 inches in diameter, and perforated in its centre so as to fit the combustion-tube. This will shield

the cork from the direct heat of the furnace, and will prevent it from being charred.

Now light the burners under the portions (*d*) and (*e*) of the tube, and heat them to *dull redness*. Then gradually extend the heat along the mixture (*c*). The intervention of the portion (*b*) will prevent the oxalic acid (*a*) from being heated, but it is better to insure this by screening it with a piece of sheet-iron or asbestos millboard.

When the portions (*c*), (*d*), and (*e*) are at a dull-red heat, and all evolution of gas has ceased, heat the oxalic acid at (*a*) gently. The gases thus evolved will drive out any ammonia gas which is still present in the tube, and will thus secure its absorption by the standard acid.

Care must be taken that no drops of liquid remain between the asbestos (*e*) and the cork. If drops are seen, gradually push the tube further into the furnace, so as to evaporate the liquid. This will prevent the risk of ammonia remaining in solution in the condensed liquid.

The acid in the bulb-tube is now poured out into a beaker, and the bulbs are rinsed out several times into the beaker. The amount of acid which has been neutralised by the ammonia is then ascertained, by titrating the free acid with normal sodium hydrate solution (**239**). Each c.c. of acid which is neutralised by the ammonia corresponds to 0·014 gram of nitrogen.

It must be remembered that unless there is an excess of standard acid in the bulb-tube at the end of the combustion, loss of ammonia will probably have occurred.

662. The Ammonia is Absorbed in Excess of Dilute Hydrochloric Acid, and is Precipitated as $(NH_4)_2PtCl_6$.

The preparation and heating of the combustion-tube is carried out precisely as is described above (**661**); but hydrochloric acid, diluted with four times its volume of water, is used for absorbing the ammonia, in place of normal sulphuric acid.

After the combustion is finished, the acid solution of ammonium chloride is transferred to a dish, and is mixed

with excess of pure platinum chloride solution; the double chloride is then estimated as is described in paragraphs **136** and **138**.

From the weight of the double chloride, the weight of nitrogen is easily calculated.

The double chloride may also be ignited, and the residual platinum weighed: and the weight of nitrogen in the double chloride may be calculated also from this weight as a control.

Estimation of Nitrogen by Kjeldahl's Process.

663. In this process, which is also suitable for moist or liquid bodies, the substance is first heated with strong sulphuric acid. The nitrogen of the organic body is thus converted into ammonium sulphate.

The acid solution is then heated with excess of sodium hydrate. The ammonia thus evolved is either absorbed in a known volume of standard acid and determined volumetrically, or it is precipitated as platino-chloride and determined gravimetrically.

Strong Sulphuric Acid, free from ammonium sulphate and from oxides of nitrogen, is required for the process. The acid can be tested by making a blank experiment with sugar instead of with urea as is described below (**664**).

664. For Practice in the Estimation, weigh out 0·7 gram of pure dry urea into a round flask of about 200 c.c. capacity, and pour in 20 c.c. of the sulphuric acid. Heat the flask upon a sand-bath until the liquid nearly boils, and maintain the heating for one hour.

Now add 8 grams of dry powdered K_2SO_4. This salt raises the temperature to which the acid may be heated without boiling, and thus completes the changes. With most organic substances, the liquid is dark-coloured before the addition of the sulphate, and at the end of the reaction becomes colourless.

By this treatment all the nitrogen of the urea will be converted into ammonium sulphate.

Dilute the cold liquid with water. Then add a moderate excess of sodium hydrate, dissolved in three times its weight of water; fit the flask with the absorption apparatus described in paragraph **138**, and proceed to distil the ammonia and to estimate its amount as is there described.

In cases where the amount of ammonia gas which is evolved is small, the flask may be connected with a Liebig-condenser, the outlet end of which simply dips into the acid contained in a flask.

The ammonia may either be received in a known volume of standard acid the excess of which is titrated after the absorption (**139**); or it may be absorbed in an excess of dilute hydrochloric acid, and estimated as is described in paragraph **138**, by conversion into the double chloride of ammonium and platinum.

Example.—The following are the particulars of an estimation.

0·8 gram of impure urea was weighed out, and was treated as is described above.

The resulting ammonia was absorbed in 100 c.c. of normal sulphuric acid.

This solution was made up to 250 c.c., and was then added from a burette to 10 c.c. of a sodium hydrate solution, which corresponds to 10·03 c.c. of the normal solution.

34 c.c. of the acid solution were required to neutralise this alkali.

Therefore the volume of acid not neutralised by the ammonia $= \frac{10{\cdot}03 \times 250}{34} = 73{\cdot}76$ c.c.

And the volume of acid neutralised by the ammonia $= 100 - 73{\cdot}76 = 26{\cdot}24$ c.c.

Therefore the weight of nitrogen in the urea $= 26{\cdot}24 \times 0{\cdot}014 = 0{\cdot}36736$ gram.

And the percentage of nitrogen in the urea $= \frac{0{\cdot}36736 \times 100}{0{\cdot}8} = 45{\cdot}92$.

Estimation of Nitrogen by Dumas' Method.

664a. This method depends on measuring the volume of the nitrogen which is evolved by the combustion of the substance.

It is applicable to the analysis of all organic compounds containing nitrogen.

The organic substance is heated with copper oxide in an atmosphere of carbon dioxide gas. Its constituent elements are then evolved as nitrogen, carbon dioxide, and steam. These products are passed through strong potassium hydrate solution into the measuring-vessel, in which the nitrogen only will be collected. The volume of gas thus obtained is corrected for temperature and pressure, and its weight is calculated.

The following materials will be required.

(a). *A Piece of Combustion-tubing*, from one-half to five-eighths of an inch in diameter, and 27 inches in length. The tube is cleaned, then sealed at one end by drawing it out in the blowpipe-flame; the other end has its edges rounded in the flame for the reception of a cork.

(b). *Sodium Bicarbonate*, pure and dry. The bicarbonate which has been prepared by the ammonia-soda process is not suitable, since it often contains ammonia.

(c). *Pure Copper Oxide*, both in the powdered and granular condition, and recently ignited. The oxide must be prepared by the oxidation of metallic copper, since that prepared from copper nitrate frequently contains nitrogen.

(d). *A Roll of Copper Foil*, or of copper-gauze, about 3 inches in length, and of such diameter as just to fit the combustion-tube. Before using the coil, it must be ignited in a current of air, and then in a stream of hydrogen gas.

665. **For Practice in the Process**, weigh out 0·3 to 0·5 gram of pure dry urea. Introduce into the end of the combustion-tube a layer of about 6 inches of the sodium bicarbonate (b), and then about 2 inches of the powdered copper oxide. Make each layer settle down compactly by tapping the tube while it is in a vertical position.

Now mix the urea intimately with the finely-powdered copper oxide (c) in a mortar, and introduce the mixture into

the tube. Rinse out the mortar with a little fresh copper oxide, and pour this also into the tube. The mixture and rinsings should occupy about 6 inches of the tube after they have been rendered compact by tapping the tube.

The mixing of the substance with the powdered copper oxide is more easily effected in the tube than in the mortar, by using a long wire bent into a corkscrew shape at its end.

Next add a layer of about 10 inches of the granular copper oxide, and then push in the copper roll. Tap the whole length of the tube, held in a horizontal position, upon the bench, so as to form a free passage along the upper part for the evolved gases. Attach a bent delivery-tube by means of a perfectly air-tight perforated cork, and slip upon the end of the combustion-tube a perforated piece of asbestos cardboard to prevent the charring of the cork. The tube is now ready for the combustion process (fig. 87, p. 410).

Lay the combustion-tube in the trough of the combustion-furnace, and proceed to heat the granular layer of copper oxide in the front of the tube. At the same time gently heat the front half of the sodium bicarbonate.

When the evolution of carbon dioxide has continued for some time, the gas may be tested to see if it is free from air.

For this purpose the gas may be passed into the special apparatus described in par. **666**.

If this apparatus is not at hand, dip the end of the delivery-tube under mercury contained in a trough. Slip over the end of the tube a test-tube, one-third of which is filled with mercury and the remainder with potassium hydrate solution.

If the bubbles escaping from the combustion-tube are completely absorbed by the potassium hydrate solution, all the air has been expelled, and the combustion may be commenced. If the bubbles are not completely absorbed, continue to heat the sodium bicarbonate, until the carbon dioxide has entirely expelled the air. Only half the bicarbonate must be heated for this purpose.

Now proceed to collect the escaping gas.

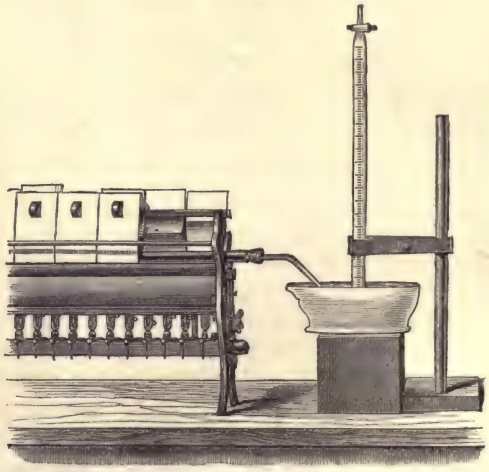
If the collecting apparatus described in par. **666** is employed, the directions given in that paragraph are followed.

Instead of using this apparatus, a graduated tube of 150 c.c. capacity may be securely clamped over the end of the delivery-tube in the mercury trough (fig. 87). Two-thirds of this tube are filled with mercury, and the remainder with a concentrated solution of potassium hydrate.

The tube may be filled and inverted as follows. Introduce the mercury first, and remove any air-bubbles adhering to the inside of the tube. Then pour in the potash solution until it reaches to within a quarter of an inch from the top of the tube; now gently pour in water until the tube is quite full. Slide a glass plate over the mouth of the cylinder, and invert it with its mouth under the mercury in the trough. Then withdraw the glass plate, and support the cylinder securely over the end of the delivery-tube. In this way the contact of the potash solution with the fingers may be avoided, since the lower specific gravity of the water causes it to float on the potassium hydrate solution.

As soon as the measuring-tube is in position, and the front part of the combustion-tube containing the copper oxide and

FIG. 87.



the copper-coil is heated to redness, gradually heat the mixture containing the substance, from the front backwards.

When the evolution of gas from the delivery-tube has

altogether ceased, heat the other half of the sodium bicarbonate at the end of the combustion-tube. The carbon dioxide thus evolved will sweep out the nitrogen which remains in the combustion-tube. Now shake the gas collected in the tube so as to bring it into contact with the caustic potash solution, and thus remove any carbon dioxide which may have escaped absorption.

When no further decrease in volume occurs, the volume of the nitrogen is read off.

If the apparatus shown in fig. 88 has been used proceed as is directed in par. **666**. If the tube shown in fig. 87 has been used, it is removed by means of a small porcelain dish filled with mercury, and placed in a large cylinder of water, which should be at the temperature of the laboratory. The mercury and caustic potash solution are allowed to fall out of the measuring-tube into the water, and the measuring-tube itself is immersed in the water.

As soon as the nitrogen has gained the temperature of the water, the measuring-tube is raised until the water is at the same level both outside and inside the tube, and the volume of the gas is then read off.

As soon as the volume of the nitrogen has been read, take the temperature of the water, and the barometric pressure. From these data the weight of the nitrogen is calculated by means of the following formula:—

$$\text{Weight of N} = \frac{v \times (p - w) \times 273 \times 0{\cdot}0012\overset{58}{\cancel{57}}}{760 \times (273 + t)} \text{ gram.}$$

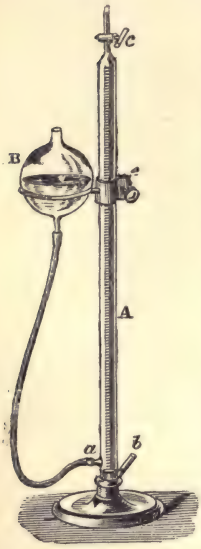
v = volume of nitrogen in c.c.;
t = temperature of the water;
p = barometric pressure, reduced to 0°;
w = the tension of aqueous vapour at $t°$;
$0{\cdot}0012\overset{58}{\cancel{57}}$ = the weight of 1 c.c. of N under normal conditions, in grams.

The above determination should be made on an organic substance, which contains no nitrogen, such as sugar. This blank experiment determines the error of manipulation, and errors due to other causes. The volume of gas found in

such an experiment should not exceed 1 c.c.; and this may be deducted from the volume of nitrogen obtained in each estimation.

666. A Form of Apparatus, in which the nitrogen may be both collected and measured, is represented in fig. 88. It consists of a graduated burette (A) of about 100 c.c. capacity, which is supported by a heavy base. This burette has a stopcock (*c*) at the top which should be lubricated with vaseline. The burette is connected by a side tube (*a*) with a reservoir (B) by means of a flexible rubber tube which has been soaked in melted paraffin-wax. There is a second tube (*b*) connected with the burette; it is inclined upwards and is about an inch and a half lower than (*a*).

FIG. 88.



Mercury is poured in through (*b*) until it rises about a quarter of an inch above the joint, and (*b*) is then closed. The bulb (B) is now charged with a solution of potassium hydrate, prepared by dissolving the solid in an equal weight of water. The stopcock (*c*) is opened, and the bulb (B) is raised until the solution fills the burette. The stopcock is now closed, and the bulb is lowered and is fixed by the clamp near the bottom of the burette.

The tube (*b*) is now opened, and the delivery-tube from the combustion apparatus is passed through (*b*) into the burette, as soon as the CO_2 which escapes is believed to be free from air. The complete freedom of the gas from air must be proved, if it has not been already established, by its complete absorption by the solution of alkali.

All air is then expelled from the tube (A) through the stopcock (*c*) by raising the bulb (B), and the process of combustion is proceeded with.

As soon as no further evolution of gas is observed from the combustion of the substance, the N is swept out from the combustion-tube by the CO_2 obtained by heating the bicarbonate, the delivery-tube is withdrawn and (*b*) is again closed.

The gas is then allowed to stand in the burette for about an hour to complete the absorption of the CO_2. The volume of the nitrogen is then read, after the bulb B has been raised sufficiently to bring the liquid in B to the same level as that in A. The nitrogen may be assumed to be dry, and its volume will require correction for temperature and pressure only.

Certain Forms of Apparatus for Collecting the Nitrogen have been devised, which render it possible to measure the gas over mercury. They consist essentially of an arrangement by which the gas can be removed from the collecting-vessel to a measuring-tube, without being accompanied by the potassium hydrate solution. By this method of measurement greater accuracy is secured than by the measurement over water or potash solution described above.

Estimation of Chlorine, Bromine, and Iodine in an Organic Substance.

667. Two methods are here described, in both of which the halogen is ultimately weighed in combination with silver.

According to the first (**668**) the substance is burnt with lime, or with soda-lime.

In the second process the substance is oxidised by heating it under pressure with strong nitric acid (**670**).

The first method is the more generally applicable, but the second method will, as a rule, be found the more convenient of the two.

668. Ignition with Lime, or with Soda-Lime.—The substance is heated strongly with lime, or with soda-lime; the halogen is thus obtained in combination with calcium.

The cool mass is dissolved in nitric acid, excess of silver nitrate solution is added to the solution, and the halogen is precipitated and weighed in combination with silver.

The process is rendered somewhat tedious, by the necessity of using a large quantity of nitric acid to dissolve the alkaline mass. This makes the operations of filtration and washing very lengthy.

The Lime or Soda-lime which is used for the combustion should be free from chloride. If it contains chloride, the amount of chlorine present must be estimated and allowed

for in the analysis, and a known quantity of the lime must always be used in the process.

Quicklime is readily prepared from marble. Break up some marble into small pieces of definite size (**142**). Introduce this into a clay crucible : and heat the covered crucible strongly in a wind-furnace for several hours. Remove the lime from the crucible as soon as it is cold, and preserve it in a well-stoppered bottle.

Soda-lime is first obtained in a granular condition (**142**). It is then heated strongly to expel moisture, and is stored in a stoppered bottle.

669. *For the Estimation*, cleanse a piece of combustion-tube about 18 inches in length. Close one end by drawing it out in the blowpipe-flame, and fuse the sharp edges of the open end in the flame.

Fill about 2 inches of the tube with the powdered lime or soda-lime : then add from 0·5 to 1 gram of the substance, finely powdered and accurately weighed. If a liquid is to be burnt, refer to *Note* 1. For practice use 0·5 gram of chloral hydrate, $CCl_3CH(OH)_2$.

Now introduce another 2 inches of the powdered lime or soda-lime ; and mix the substance with this portion by pushing down into the tube a long bright piece of wire, which is bent like a corkscrew at its end, and turning this wire round in the powder and substance. Almost fill the tube with more granular lime or soda-lime, and then insert a loose plug of asbestos.

Draw off the open end of the combustion-tube into a narrow tube, and bend this tube obliquely as is shown in fig. 62 (p. 138). Lay the tube in the trough of the combustion-furnace, just immersing its open end in water contained in a small beaker.

Now heat the front portion of the tube, containing the granular lime, to redness. When the lime is red hot, gradually extend the heat to the mixture. Any substance which escapes complete decomposition will be seen to escape

into the water in the beaker, and may be tested for the halogen.

As soon as the decomposition is complete, remove the combustion-tube, cut off its narrowed end, and transfer its contents to a beaker. Rinse out the tube with dilute nitric acid into the beaker. If iodine is present, refer to *Note* 2. Add more nitric acid, and stir until the lime is completely dissolved. Filter off the particles of carbon and glass, and add an excess of silver nitrate solution. Filter off, dry, ignite, and weigh the precipitate (**113–116**).

Instead of weighing the silver compound, the nitric acid solution may be neutralised, and may then be titrated by standard silver nitrate solution (**304**).

Note 1.—**A Volatile Organic Liquid** is dropped into the combustion-tube in a small bulb (**656**) after the first 2 inches of lime powder have been introduced; or it is treated as in par. **657**.

Note 2.—**Iodine** may be liberated during the combustion. It must be converted into hydriodic acid by means of sulphurous acid, before adding nitric acid and precipitating with silver nitrate solution.

Iodine may also be partially converted into iodate: hence sodium sulphite must be added to reduce this to iodide and thus render it precipitable by silver nitrate.

670. Carius' Method for Estimating the Halogens.—In this method the organic substance is mixed with fuming nitric acid and silver nitrate, and is then heated for about two hours in a sealed glass tube. The halogen is thus obtained in combination with silver, and is weighed in this form.

The Process of Estimation.—Cut off a piece of *thick-walled* combustion-tube, about 20 inches in length. Seal up one end in the blowpipe-flame, being careful to make the end strong and round in shape, and to anneal the glass well by allowing it to cool down slowly in the luminous flame.

Next weigh out accurately about 0·5 gram of the substance in a thin weighed glass bulb-tube, using chloral hydrate, $CCl_3.CH(OH)_2$, for practice.

The bulb-tube is made from a thin-walled ignition-tube, three-sixteenths of an inch in diameter, by heating its closed end in the flame, and blowing it out into a bulb about half an inch in diameter. When the tube is cold, weigh it. Then introduce the substance. Draw off the upper part of the tube by holding it in a blowpipe-flame, so as to seal the tube, and weigh the two parts of the tube with the inclosed substance. The gain in weight of the tube gives the amount of substance taken. Reserve the portion of the glass drawn off from the bulb, for a subsequent weighing.

Push the bulb containing the substance carefully to the closed end of the combustion-tube. Introduce about twice as much solid silver nitrate as is theoretically required to furnish sufficient silver to combine with the halogen. Then pour in fuming nitric acid, of 1·5 specific gravity: about 3 c.c. of the acid being added for each 50 c.c. capacity of the combustion-tube. Acid of 1·42 specific gravity will serve for some substances.

Now draw out and seal the open end of the tube. For this purpose hold the tube in a slanting position, so that its contents remain undisturbed at the bottom; and gradually heat the tube at about 3 inches from its open end. Rotate the tube continually in the flame, until its sides soften and thicken and begin to fall together. The upper part may then be gradually drawn off, leaving a thick-walled sealed capillary end, which is annealed by cooling it at first in the luminous flame, and finally in the air.

The tube is now sharply shaken so as to break the small bulb, and is then heated in the air-bath.

The Air-bath (fig. 89) is a stout sheet-iron box 22 inches in length. Four pieces of iron gas-pipe, open at both ends, and 1½ inches in internal diameter, pass through holes in the ends of the box. The projecting ends of these pipes have a screw-thread turned on their surface, and a lock-nut is screwed upon each of them in order to keep the tube in position.

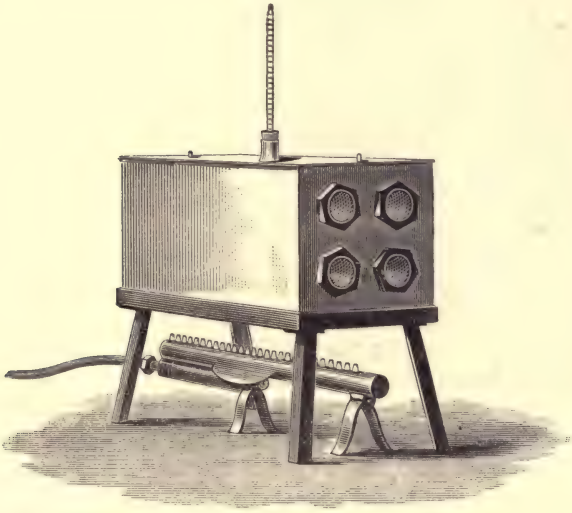
A cork bearing a thermometer is inserted into a hole in the top of the bath; this serves to register the temperature of the interior. A suitable Fletcher-burner for heating the bath uniformly is shown in the figure.

When the bath is in use, a sheet-iron cover is placed over it; the top of this cover rests upon the top of the bath; it is open at the bottom, and the sides and ends are half an inch distant from the bath itself. This cover is kept in position by two pins, which are shown on the upper surface of the bath, and which pass through corresponding holes in the top of the cover. The cover insures a more uniform temperature in the bath, and prevents the glass and acid from being scattered about, if a tube should burst.

It will be seen that four glass tubes can be heated at the same time in the air-bath.

Place the sealed tube in one of the iron tubes of the air-bath. It is well to push the glass-tubes into a wrought-iron tube closed at one end, and to place both together in the

FIG. 89.



broader tube of the air-bath. This affords security from injury, when the tube is being handled after it has been heated.

Now put the cover on the bath, and light the burner. Watch the thermometer carefully, and allow the temperature to rise until it reaches 150°; then maintain the bath at this temperature for two hours by properly regulating the

supply of gas to the burner (*Note* 1). The temperature of 150° is only mentioned as that which is frequently suitable. Some substances require a temperature of 250°, while others are decomposed at temperatures below 150°.

Now allow the bath and tube to become *quite cold*. Then take out the tube. If the tube is not provided with a protecting wrought-iron jacket, it must be thickly wrapped in a cloth in order to guard it against any shock, and to prevent accident in case the tube should burst.

Hold the tube in an oblique position with the capillary end upwards: rinse out any particles of silver salt from the capillary by means of the liquid, and allow the liquid to drain away completely from the upper part of the tube. Then carefully warm the capillary end of the tube, so as to drive out any liquid which may have lodged there: and gradually heat the extreme end of the capillary to redness.

As soon as the glass has become soft, the gases will escape under pressure. When the issue of gas ceases, cut off the end of the tube with a file, and rinse out the contents with water into a beaker. Remove and wash any large pieces of the glass bulb, dry them in the steam-oven, and weigh them together with the end which was drawn off from the glass bulb on sealing it.

Neutralise most of the free acid in this liquid with sodium hydrate solution, and filter off (*Note* 2), wash, dry, and weigh the silver salt (**113**). The weight of the silver chloride will be increased by the small pieces of glass from the fractured bulb; their weight must accordingly be deducted from that finally obtained for the precipitate. The weight of this glass is found by deducting from the weight of the original empty bulb, the weight of the larger fragments and end which was obtained above.

Note 1.—When the substance requires to be heated for a long time with the acid to a high temperature, it is best to allow the gases to escape from the *cold tube* once or twice during the process of heating, then to seal up the tube again and proceed with the heating. This precaution will often save the tube from bursting. In an ordinary determination the tube may be sealed up and re-heated, if there is any doubt about the oxidation of the substance being complete after the capillary has been opened.

Note 2.—If iodine was present in the organic substance, the silver nitrate and silver iodide sometimes fuse together into a yellow mass. The silver nitrate must then be removed from the mass, by heating it in the diluted liquid for one or two hours.

Estimation of Sulphur in an Organic Substance.

Several methods serve to oxidise the sulphur in an organic substance into sulphate: the sulphur can then be precipitated and weighed as barium sulphate.

671. Oxidation by Nitric Acid, as in Carius' method for determining the halogens (**670**), is suitable for the estimation of sulphur. The substance is heated with strong nitric acid of 1·5 specific gravity, as has been already described (*loc. cit.*), the silver nitrate being omitted. The sulphur is thus converted into sulphuric acid.

When the tube is cold, its contents are rinsed into a porcelain dish. The excess of nitric acid in the liquid is removed by evaporating it nearly to dryness on the water-bath, after adding excess of hydrochloric acid, and some sodium chloride to fix the sulphuric acid. The liquid is then diluted, and the (SO_4) is estimated as $BaSO_4$ (**96**).

672. The methods of estimating sulphur in coal (**475**), and sulphur in blende (**105**), are also applicable to many organic substances.

Estimation of Phosphorus in an Organic Substance.

673. If an organic substance containing phosphorus is subjected to the processes described above (**671, 672**), the phosphorus is converted into phosphoric acid. The solution obtained by these processes may then be rendered alkaline with ammonium hydrate, and the phosphate may be precipitated with magnesia mixture (**132**), and estimated as $Mg_2P_2O_7$ (**131**).

Determination of the Molecular Weight of an Organic Compound.

Three methods are described below.

The first two are usually applied to substances which are not volatile without decomposition, and are either basic or acid in nature. They depend upon forming definite bodies of a saline nature.

The third method, depending upon the lowering of the freezing-point of a solvent in which the substance is dissolved, is of general application to organic and inorganic substances.

A fourth method, which depends upon determining the vapour density, is applicable to volatile compounds only (**736**).

674. Determination of the Molecular Weight of an Organic Acid.—The molecular weight can be determined, in the case of certain organic acids, by preparing an insoluble metallic salt from the acid, and determining the weight of the metal in a known weight of the pure salt. Since silver is a monad metal, and forms many insoluble salts, it is generally selected: but in certain cases the barium or lead salt is prepared.

As an illustration, we will suppose that the combustion of pure acetic acid has given the empirical formula CH_2O. It is evident that either this formula, or some multiple of it, will represent the molecule of acetic acid.

Only one silver salt can be obtained; hence acetic acid is inferred to be monobasic.

The molecular weight of acetic acid is then determined by preparing the pure dry silver salt, igniting a known weight of this salt, and weighing the residual silver. From this result the weight of the silver salt which contains 107·98 of silver may be obtained by calculation. This will be the molecular weight of the silver salt. By subtracting from this molecular weight the atomic weight of silver and adding that of hydrogen, the molecular weight of the acid will be obtained.

Example.—Two grams of pure dry silver acetate gave on ignition 1·2934 grams of silver.

Now the weight of silver thus found will stand in the same ratio to the atomic weight of silver, as the weight of the silver acetate, which was taken, does to the molecular weight of silver acetate.

Therefore the molecular weight of silver acetate $= \frac{107{\cdot}98 \times 2}{1{\cdot}2934} = 166{\cdot}97$.

And the molecular weight of the acid $= 166{\cdot}97 - 107{\cdot}98 + 1 = 59{\cdot}99$.

This corresponds to the molecular formula $C_2H_4O_2$.

In the case of a polybasic acid, such as meconic acid, more than one silver salt may usually be prepared. These salts will contain different proportions of silver; but from a study of the proportions of silver, the basicity of the acid may usually be inferred.

For Practice in the Estimation, prepare some pure silver succinate, by adding a moderately strong solution of silver nitrate to sodium or ammonium succinate solution. Filter off the silver succinate, wash it free from dissolved salts, and dry it at as low a temperature as possible.

Weigh out accurately about 1 gram of the silver succinate, and ignite it, *very gently* at first, in a covered weighed porcelain dish. Finally keep it at a red heat for a short time; and repeat the process of heating, until the weight of the residual silver is constant.

The molecular weight is then calculated as has been already described. But assuming that succinic acid is diabasic, it is evident that $2 \times 107{\cdot}98$ must be subtracted from the molecular weight of the silver succinate, and 2×1 must be added to the remainder, in order to obtain the molecular weight of the acid.

675. Determination of the Molecular Weight of an Organic Base.—Certain organic bases, notably the alkaloids, combine with hydrogen chloride and platinum chloride to form double salts. These resemble in constitution the double chloride of ammonium and platinum, $2(NH_3HCl).PtCl_4$, the organic base taking the place of the NH_3.

The molecule of the double salt therefore usually contains two molecules of the organic base; and if R represents a

monad organic base, the general formula of the double salt is $2(RHCl).PtCl_4$. When the molecular weight of this organic double salt is known, the value of R can be calculated, since the weight of the other elements present in the molecule is known and can therefore be subtracted.

The method of procedure is identical in principle with the one last described (674). A suitable quantity of the pure dry double salt is weighed; this is strongly ignited in the air until it is free from carbon, and the weight of the residual platinum is ascertained.

The molecular weight of the double salt is then obtained from the following proportion statement:—

The weight of Pt found : atomic weight of Pt :: weight of double salt used : molecular weight of double salt.

The molecular weight of a monad base is then found by subtracting from the molecular weight of the double salt the weight represented by H_2PtCl_6, and dividing the remainder by 2.

Example.—2·32 grams of caffeine platino-chloride yielded 0·57 gram of platinum.

Hence the molecular weight of the double salt $= \frac{195{\cdot}5 \times 2{\cdot}32}{0{\cdot}57} = 795{\cdot}7$.

Therefore the molecular weight of caffeine $= \frac{795{\cdot}7 - 410{\cdot}2}{2} = 192{\cdot}7$.

For Practice in the Estimation, dissolve some pure strychnine in dilute hydrochloric acid, and add to the solution a moderate quantity of platinum chloride solution. A yellow or orange precipitate of the double salt will form. Filter this off, wash it about six times with alcohol, and dry it in the steam-oven.

Weigh out 1 gram of this double salt into a porcelain crucible; ignite it gently at first, and then strongly. Continue the ignition until all the carbon is burnt away; stirring occasionally so as to promote the combustion of the carbon. When the weight of the residual platinum is constant, the molecular weight of the alkaloid may be calculated as is described above.

676. The Raoult Method.—The molecular weights of many substances, which cannot be determined by the preceding methods (**674, 675**), or by their vapour density (**735–742**), can be determined by the lowering of the freezing-point of the solvent employed for their solution.

The method depends upon the fact, that if quantities of different substances, which are proportional to their molecular weights, are dissolved in equal amounts of the same solvent, the freezing-point of the solvent is in every case *depressed* to the same extent. This depression varies directly with the amount of substance used, and inversely with the amount of solvent.

Hence the depression of the freezing-point, which is caused by dissolving the molecular weight in grams of a body of known molecular weight in a known weight of the solvent, is first ascertained. The molecular weight of any other substance can then be readily found, if a known weight of that substance is dissolved in a known weight of the same solvent, and the depression of the freezing-point which is thus caused is noted.

The Formula required for Calculating the Molecular Weight is deduced as follows:—

If A = the *Coefficient of Depression*, or the depression of freezing-point produced by dissolving 1 gram of the substance in 100 grams of the solvent;

M = the molecular weight of the substance dissolved;

T = the *Molecular Coefficient of Depression*, or the depression of freezing-point produced by dissolving the molecular weight of the substance in grams in 100 grams of the solvent;

$$\text{Then } T = M \times A. \quad . \quad . \quad . \quad . \quad (1.)$$

If P = the weight in grams taken of the substance, the molecular weight of which is required;

Q = the weight used of the solvent, for which T is known;

K = the depression of freezing-point obtained in the experiment;

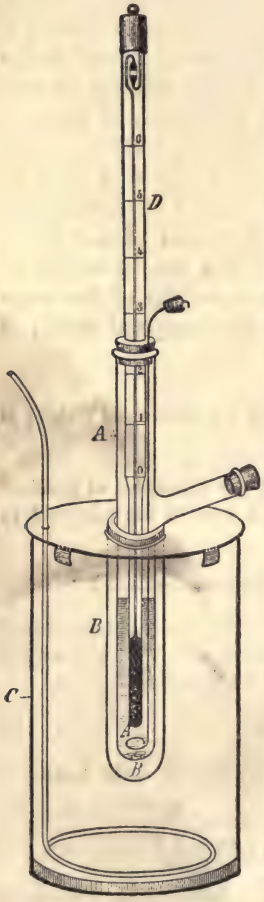
Then the *Coefficient of Depression* (A) can be found from the proportion

$$\left.\begin{matrix} P : 1 \\ 100 : Q \end{matrix}\right\} :: K : A ; \qquad \text{Or } A = K\frac{Q}{P \times 100} \quad . \quad . \quad . \quad (2.)$$

$$\text{Now } M = \frac{T}{A} \text{ from (1.)}$$

$$\text{Therefore } M = \frac{T \times P \times 100}{K \times Q} \quad . \quad (3.)$$

FIG. 90.



The Process of Determination of the Depression of the Freezing-point is most conveniently carried out in the apparatus of Beckmann (fig. 90).

The glass tube A receives a thermometer D, which can indicate hundredths of a degree (*Note*); it also contains a stirring-rod made of stout wire. A weighed quantity of the solvent is introduced into the tube A, which is then placed in a somewhat wider tube B. An air-jacket is thus formed between the tube A and the outer vessel C. This external vessel contains either water or a freezing-mixture, the temperature of which must be from 2° to 5° below the freezing-point of the solvent.

The thermometer is now observed while the liquid is kept constantly stirred, small pieces of platinum foil being introduced into the inner tube A to aid in the thorough mixing. At first the temperature sinks below the true freezing-point, but it rises to the correct temperature as soon as the solid begins to separate.

When the freezing-point of the solvent has been ascer-

tained, a known weight of the substance, of which the molecular weight is required, is introduced through the side tube into A. The liquid is then thoroughly stirred, and the temperature of freezing is again noted. The "ice" now forms at a lower temperature than before, and the difference between the two temperatures gives the lowering of the freezing-point (K).

When concentrated solutions are employed, over-cooling frequently takes place, and a large quantity of "ice" separates suddenly. This has the effect of making the observed freezing-point too low. In such cases most of the ice must be allowed to melt, and when only a small quantity is left, the apparatus must be again immersed in the cooled outer vessel.

Calculation of Molecular Weight.—The molecular weight (M) is calculated by means of the formula given on p. 424.

If T is unknown, it can readily be ascertained by dissolving a definite quantity of a substance of known molecular weight in a weighed quantity of the solvent. The value of T is then calculated from the relation $T = M \times A$.

Note.—The capillary tube of the thermometer usually has a bulbous space at the top, which can receive some of the mercury, and thus enable the height of the mercury-thread to be adjusted to suit various freezing-points.

For Practice in the Method use 6 grams of pure cane-sugar, or of glucose. Dissolve this in 50 grams of water, for which T = 19. Introduce into the outer vessel a mixture of ice and salt.

Example.—12·616 grams of glucose were dissolved in 92·25 grams of water. The freezing-point of the water was depressed 1·45° C., and T = 19.

By equation (3), page 424,

$$\text{The molecular weight} = \frac{T \times P \times 100}{K \times Q} = \frac{19 \times 12{\cdot}616 \times 100}{1{\cdot}45 \times 92{\cdot}25} = 179.$$

PART V.

VOLUMETRIC ESTIMATION OF GASES AND VAPOURS.

679. Introductory Remarks.—The measurement of gases and vapours, and the quantitative analysis of gaseous mixtures, usually involve special methods, and are therefore described in a separate part of the book.

Some methods for estimating dissolved gases by gravimetric processes, and by titration with standard solutions, have been already described. Certain gases may also be estimated by absorption in a standard solution, upon which they can produce a definite chemical effect. But the determination of the quantity of a gas very frequently involves either the direct measurement of its volume, or the indirect measurement by noting the loss of volume resulting from the absorption of the gas.

When the volume of a gas is dealt with, not only is special apparatus required, but special corrections and calculations are usually requisite to make the results of the estimations comparable. These corrections are rendered necessary by the very considerable effect which changes of temperature and pressure, and the presence of varying amounts of moisture, exert upon the volume of a gas.

Since these particular characters also apply to vapours, it has been found convenient to describe vapour density determinations in connection with the estimation of gases.

The processes of measuring and analysing gases, which are described in detail in this Section, involve the use of com-

paratively cheap and simple apparatus. They also either dispense with the use of mercury, or require it only in small quantity.

The volume of the gas is frequently measured over water. This introduces a certain amount of error, since all gases dissolve in water to a varying extent. The results obtained by these processes are therefore somewhat inferior in accuracy to those yielded when the gases are measured over mercury only. But the simpler method of measurement over water is now very generally adopted for certain gases, and is found to furnish results of a very satisfactory nature, when a sufficient volume of gas can be employed, and proper precautions are taken.

680. Reference Books.—For the description of the larger and more costly forms of gas-apparatus, and for directions regarding their use, reference may be made to *Sutton's Volumetric Analysis.*

The following books will also be found useful for purposes of reference, and for gaining fuller information :—

Bunsen's Gasometrische Methode } or English
Winkler's Technische Gas-analyse } Edition.
Winkler's Technical Gas-analysis ;
Hempel's Gas-analysis.

Calculation of Volume under Normal Conditions.

681. The molecules of a gas or vapour tend to recede from one another, under increased temperature or decreased pressure, to a far greater extent than do the molecules of a liquid or a solid.

The volume of a definite weight of any gas therefore varies appreciably with comparatively small changes of temperature and pressure. If the gas is in contact with water, its volume will also be increased by the presence in it of aqueous vapour.

The volume of a gas is usually measured at the temperature of the laboratory, and at the atmospheric pressure. Since, however, this temperature and pressure are subject to variation, the conditions under which different measurements are made may be dissimilar. The gas will also vary by being either dry or moist, according to the liquid over which it is measured.

In order to make different measurements of the volumes of gases comparable one with another, or to be able to calculate the weight of a gas; it is, therefore, usually necessary to ascertain by calculation the volume which the gas would occupy in a dry state, and at 0° C. and 760 mm. pressure. This is usually termed "the volume under normal conditions."

682. Calculation of the Volume of a Gas under Normal Pressure.—The volume of a gas varies inversely as the pressure which is exerted upon it.

Therefore, if:—

v = the observed volume of the gas,
p = the observed barometric pressure,
V_n = its volume at 760 mm. pressure (normal),

$$\text{Then } V_n = \frac{p \times v}{760}.$$

This formula supplies the "Correction for Pressure."

Note.—In very accurate determinations, the height of the barometer should be reduced to its equivalent at 0° C. If H represents height of the barometer in mm. at 0°, h the observed height, and t the temperature; then $H = \frac{5508 \times h}{5508 + t}$.

683. Calculation of the Volume of a Gas at Normal Temperature.—A gas expands by one two-hundred and seventy-third (= 0·003665) of its volume at 0° C., for each degree Centigrade rise in its temperature.

Therefore, if:—

v = the observed volume of the gas,
t = the observed temperature,
V_o = its volume when reduced to 0° C. (normal),

$$\text{Then } V_o = \frac{273 \times v}{273 + t} = \frac{v}{1 + 0{\cdot}003665t}.$$

This formula supplies the "Correction for Temperature."

684. Calculation of the Volume of a Gas in the Dry Condition.—When a certain volume of a gas is saturated with moisture at the same temperature, it always contains the same quantity of moisture.

The water-vapour which is mingled with the gas exerts a certain pressure, which is commonly termed the *Tension of Aqueous Vapour.*

This pressure increases with the temperature. It is expressed in mm. of mercury, and has been very accurately determined for each degree of temperature (**779**).

The tension of aqueous vapour acts in opposition to the barometric pressure, and tends to increase the volume of a gas. Hence correction is made for its effect upon the volume of the gas, by subtracting its amount from the barometric pressure. Thus, if w is the tension of aqueous vapour in a volume of moist gas under pressure p, the true pressure on the gas $= (p - w)$.

685. General Formula for the Calculation of the Volume of a Gas under Normal Conditions.—The three preceding corrections may be embraced in the following formulæ, in which V represents the volume of the gas at normal pressure and temperature and corrected for moisture if necessary.

(1). For a dry gas, $V = \frac{p \times 273 \times v}{760(273 + t)} = \frac{p \times v}{760(1 + 0{\cdot}003665t)}$.

(2). For a moist gas,

$$V = \frac{(p - w) \times 273 \times v}{760(273 + t)} = \frac{(p - w) \times v}{760(1 + 0{\cdot}003665t)}.$$

These formulæ serve to correct the volume of a gas for temperature, pressure, and aqueous vapour.

The factors which are given in the Appendix (**778**) will be found useful for quickly calculating the normal volume.

Calibration of Measuring-tubes.

686. The graduations of measuring-tubes for gases represent either absolute c.c. and fractions of c.c. capacity (**203**), or millimetres length on the tube.

If they represent millimetre spaces on the tube, the value of the graduations in terms of c.c. must be determined. Since a glass tube always varies in diameter in different parts, it follows that equal lengths on different parts of a graduated tube do not correspond to equal capacities; hence it is necessary to calibrate the tube throughout its length.

Two liquids are in common use for calibrating measuring-tubes, namely, mercury and water.

687. Calibration of the Measuring-Tube by means of Mercury.—For this purpose the tube is supported vertically, with its open end upwards; and successive equal weights of mercury are poured in from a little tube of about 4 c.c. capacity. The space in the tube which is occupied by each portion of mercury is noted by means of the graduations, and the true volume of the mercury is calculated from its weight. The capacity of the tube at every graduation can then be determined by calculation.

688. *Calibration of the Measuring-tube used in Meyer's Vapour-density Apparatus.*—Fix the tube in a wooden clamp and make it truly vertical by hanging a plummet beside it, and setting the side of the tube parallel with the line of the plummet (fig. 91).

Make a small vessel about 4 c.c. in capacity by drawing out a piece of glass tube at one end in the blowpipe-flame, and grind the edge of the open end perfectly level and smooth. Hold this vessel in a little wooden clamp (fig. 92), and fill it with mercury from a bulbed-tube, which can be closed by means of a stopcock.

As soon as the vessel is quite filled, slide a glass plate

along the ground edge of the tube; this will remove the excess of mercury, and will leave the mercury surface exactly level. Now pour the mercury from the vessel into the graduated tube. Remove the air-bubbles, which adhere to the inside of the tube, by means of a thin piece of lance-wood

FIG. 91.

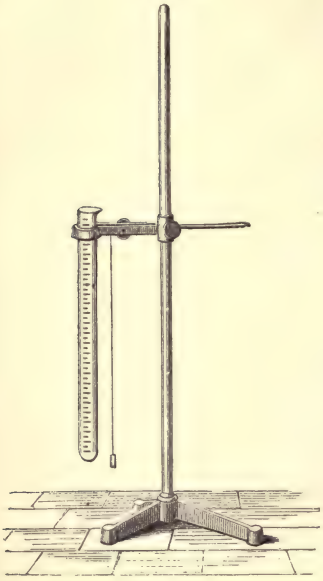
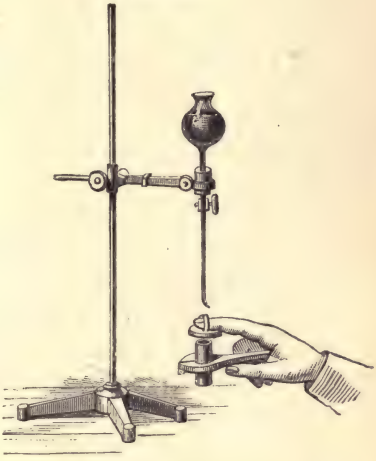


FIG. 92.



or whale-bone; and then read the level of the highest point of the meniscus of the mercury by means of the graduations.

Fill the vessel repeatedly, and empty it into the graduated tube, and carefully read the level of the mercury after each addition.

These readings are most accurately taken by means of a cathetometer.

The Cathetometer consists of a horizontal telescope sliding on a vertical stem. The telescope may be moved vertically on the stem by means of a screw adjustment. The telescope is set horizontally by means of a spirit-level before each reading. The point of intersection

of the cross-wires of the telescope is then focussed upon the highest point of the mercury meniscus. Since the telescope is horizontal, errors of parallax are avoided in reading the height of the mercury.

If the cathetometer is not employed, great care must be taken that the eye is placed on the same level as the mercury surface. This is best secured by holding a small vertical mirror behind the tube, in which the reflection of the eye and of the meniscus can be seen. The reflection of the highest point of the meniscus must be seen at the centre of the pupil of the eye during the reading. A piece of cardboard may be slipped down behind the tube until its shade sharply defines the mercury surface.

The weight of mercury which fills the small vessel is now accurately determined, and the temperature of the air is noted. The capacity of the tube, between the successive readings, will then be given in c.c. by the following expression:—

$$V = \frac{g \times (1 + 0{\cdot}000143t)}{13{\cdot}596},$$

in which (g) represents the weight of the mercury in grams, and (t) the temperature at which the calibration is made; while 0·000143 is the coefficient of expansion of mercury and 13·596 is its specific gravity.

The method of calculating the capacity of the tube at each graduation will be understood by reference to paragraph **218**. But the "error of meniscus" (**689**) must be added to each volume thus obtained, if the tube is used for measuring gas over mercury.

These capacities are practically correct for measurements of gas over water.

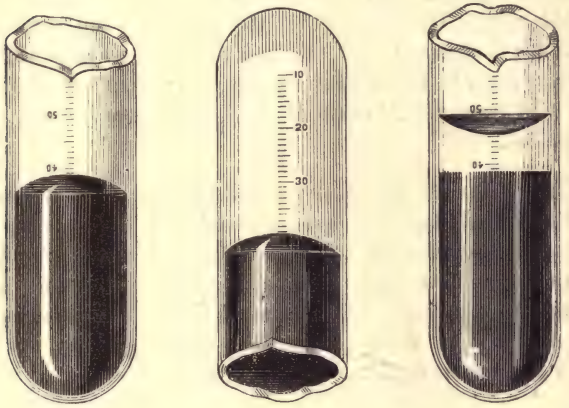
689. Error of Meniscus.—During the calibration, the convexity of the mercury is turned towards the open end of the tube (fig. 93); while in the measurement of a gas the convexity will be in the opposite direction (fig. 94). Hence it is obvious that the volume of mercury measured during the calibration, in the inverted tube (fig. 93), is less than the volume of the gas which is measured when the mercury stands at the same division in the erect tube (fig. 94).

The correction which is thus rendered necessary is made by reading off the position of the meniscus in the tube (fig. 93), and then introducing a few drops of mercuric chloride solution. This solution overcomes the repulsive action of the glass upon the mercury, and immediately causes the mercury surface to become flat (fig. 95). The level of the mercury surface is then again read off.

Thus in fig. 93, the top of the meniscus just touches division 39; whereas in fig. 95 the mercury stands at 38·7. This shows a depression of 0·3.

If gas were measured in the tube, and the mercury stood at division 39 (fig. 94), and if it were possible to overcome the repulsive action of

FIG. 93. FIG. 94. FIG. 95.



the glass as before, the horizontal surface would stand at 39·3. Therefore the volume between 38·7 and 39·3, that is 0·6, would escape measurement. Hence 0·6 is called *the Error of Meniscus*.

In practice, therefore, this error is equal to the difference between the reading of the convex surface of mercury, and the reading when the surface is levelled by means of mercuric chloride solution, multiplied by two. This number must be added to the calculated capacity of the tube when the volume of the gas is read over mercury. Allowance is usually made for the error in calculating the calibration value of the tube.

If the tube is to be used for the measurement of gas over water instead of over mercury, the capacity actually observed in the calibration with mercury should be taken, without correction for meniscus. The convex surface of the mercury during calibration will almost

coincide with the concave water-surface, when the tube is used in an inverted position, and hence the above error will be absent.

690. *Calibration of the Measuring-tube in the Lunge Nitrometer* (**714**).—The measuring-tube of the Lunge apparatus may be readily calibrated by detaching it from the apparatus, stopping the bottom, and then filling the tube up to the commencement of the graduations with mercury. The tube is clamped vertically (fig. 91, p. 431). Successive equal volumes of mercury are then added from the small tube (fig. 92, p. 431), and the readings are taken as has been described above. No correction for meniscus is necessary in this case. The capacity of the tube between successive readings is obtained from the formula given on page 432.

Care must be taken that *very small* measures of mercury are used from 2 c.c. to zero, if small volumes of gas are to be measured.

Calibration of Measuring-tubes by means of Water.—This method depends upon ascertaining the capacity of successive portions of the tube by introducing into it, or allowing to flow from it, known weights of water at a known temperature. The volume of the water is then calculated, and from these volumes the capacity of the tube to each graduation may be calculated (**218**).

691. *Calibration of the Hempel Burette* (fig. 96, p. 436).—Since the measurement of gas in this burette is made over water, the calibration of the measuring-tube should be made by means of that liquid.

Disconnect the measuring-tube, and attach to the lower end of it, by means of a rubber joint, a glass tube about 4 inches in length with a stopcock in its middle. The end of this tube must be drawn out into a fine jet. The stopcock must be *rigidly* attached to the measuring-tube, by means of thick rubber tubing bound with thin copper wire: the ends of the glass tubes must touch one another within the joint. The jet should be bent downwards, so as to deliver into a vessel held beneath it.

Now completely fill the measuring-tube and stopcock-tube with distilled water at the temperature of the room, which must be carefully noted. Take care that all air-bubbles are excluded. Then draw off successive portions of water, of 5 c.c. each, into a stoppered weighing-bottle: the lowest point of the surface-meniscus of the water (fig. 67, p. 158) being read.

When the top of the tube is being calibrated, smaller volumes of water than 5 c.c. must be drawn off, if the measuring-tube is to be used for small volumes of gas.

Weigh each of these portions, noting down the weight of the water against the reading on the tube. The bottle must be carefully dried after each weighing.

From the weights of water thus obtained, the corresponding absolute volumes are calculated, by applying the correction for expansion of water from the Table (**775**). Thus, if the first 5 c.c. weighed 4·86 grams at 20° C., its absolute volume would be $4{\cdot}86 \times 1{\cdot}00157 = 4{\cdot}868$ c.c.

It will be seen that this calibration is similar to that which is employed for the calibration of the burette (**217**), and the calculation of the capacity is made as is directed for the burette (**218**).

Caution.—It should be remembered that in all measurements in which water and similar liquids are used, it is necessary that a certain time should be allowed for the liquid to drain down the sides of the measuring-tube. The time will vary from 0·5 to 5 minutes, according to the nature of the liquid. For ordinary operations with water 2 minutes will suffice.

THE HEMPEL GAS-APPARATUS.

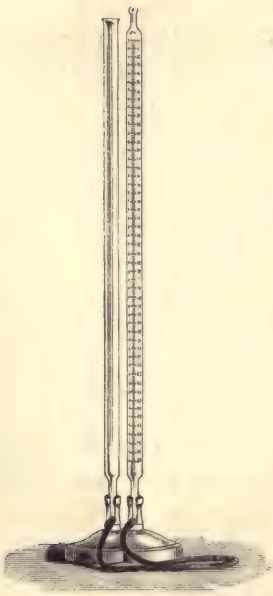
692. In this apparatus (**693**) the gas is measured over water, or some aqueous solution. The apparatus consists of two parts, the Burette, which includes a measuring-tube and a pressure-tube, and the Pipette.

A special form of Burette must be used when the gas cannot be measured over water on account of its solubility (**697**).

693. The Hempel Gas Burette (fig. 96) consists of two glass tubes. One of these is plain, and is called the *Pressure-tube*. The other, known as the *Measuring-tube*, is graduated into 100 c.c. with 0·2 c.c. divisions.

The *Pressure-tube* is cylindrical throughout, and is widened at the top. The *Measuring-tube* is contracted at the top, and terminates in about 1 inch of thick-walled capillary-tube. It is calibrated as is directed in paragraph **691**.

FIG. 96.



Each of these tubes is fitted into a slot in a semicircular weighted wooden foot.

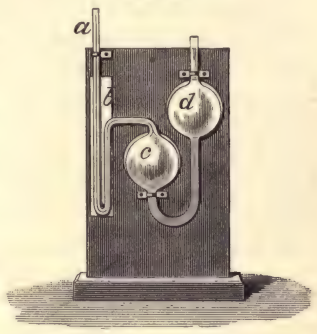
The lower ends of the tubes are contracted in diameter, and are bent at right angles, and these ends are connected with one another by a few feet of narrow rubber tubing. It is convenient to have this rubber tube divided in the middle, and joined by a short piece of glass tube, since this facilitates the cleaning of the burette.

694. The Hempel Gas Pipette.—The burette is almost always used in connection with the Hempel-pipette. The simplest form of this pipette is shown in fig. 97. By using a series of these pipettes a gaseous mixture can be submitted to the successive action of suitable absorbent reagents (**698**), and the proportions of the constituent gases can be ascertained.

The pipette (fig. 97) consists of two connected bulbs, (*c*)

and (*d*), which contain the absorbent liquid. The bulb (*c*) terminates in a U-shaped capillary tube (*a*). Behind this tube is a white porcelain scale (*b*), which renders the thread of liquid in the capillary visible when the pipette is in use.

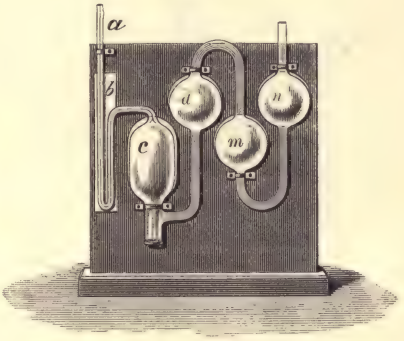
Fig. 97.



Another form of absorption-pipette is shown in fig. 98. The bulb (*c*) is cylindrical in form, and is tubulated below for admitting a solid absorbent.

Both these forms of pipette may be fitted with the two extra bulbs (*m*, *n*) shown in fig. 98. These are partially filled with water, which prevents the air from coming into contact with the absorbent. The water also prevents the escape of irritating vapour from a volatile absorbent.

Fig. 98.



695. Fitting together the Hempel Apparatus.—The burette and pipette are connected, as is shown in fig. 99. Short pieces of rubber tube, each carrying a spring clip, are slipped upon the capillary top of the measuring-tube, and upon the tube (*a*) of the pipette. These rubber joints are tightly bound with wire upon the glass, if necessary, to make them gas-tight. A single clip upon the measuring-tube (*b*) will usually be found sufficient.

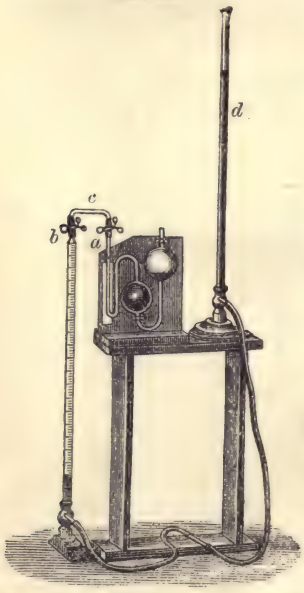
A piece of thick-walled glass tube, 1 millimetre in internal

diameter and about 8 inches in length, is then bent twice at right angles (*c*, fig. 99). Each end of this tube is pushed into one of the pieces of rubber tubing bearing the clips. This enables the connection between the absorption-pipette and the measuring-tube to be opened at pleasure, by releasing the clips. It also enables the measuring-tube and the absorption-pipette to be disconnected, without allowing their contents to come into contact with the atmosphere.

696. Manipulation of the Hempel Apparatus.—The following is a general description of the method of using the apparatus.

Taking the Sample for Analysis.—Disconnect the pipette (*a*), leaving the tube (*c*) and the rubber tubes and clips attached to the measuring-tube (*b*). Raise the pressure-tube (*d*), which has been filled with water; open the pinch-cocks, and pour water into the pressure-tube until the measuring-tube is full of water, and the water begins to flow over.

FIG. 99.



Now close the rubber tube (*a*) by the clip, squeezing the end of the tube between the finger and thumb to exclude air, while connecting it with the vessel containing the gas which is to be examined. Place the pressure-tube (*d*) at a lower level than the measuring-tube (*b*), and open the clip again. The gas will thus be drawn over into the measuring-tube.

It is convenient to use precisely 100 c.c. of gas for the analysis, since the volumes obtained in the analysis then represent percentages. This volume is secured as follows.

As soon as about 110 c.c. of gas have entered the measuring-tube, close the rubber tube by the clip. Now close the long rubber-tube by pinching it with the fingers. Raise the pressure-tube, and by relaxing the fingers, allow water to flow into the measuring-tube until it precisely reaches the 100 c.c. graduation. Then at once arrest the inflow of water by pressure of the fingers on the rubber tube. Now open the top of the measuring-tube, by relaxing the clamp for a moment, to bring the gas to atmospheric pressure. Next proceed to verify the volume of the gas, when the water is at precisely the same level in both tubes.

The temperature of the room and the barometric pressure need not be noted in ordinary analyses, since these conditions do not alter appreciably during a series of estimations. If for any reason, however, the absolute volume of the gas is to be found under normal conditions, or its weight is to be calculated, the thermometer and barometer must be read.

Charging the Pipettes.—Now charge each pipette with the absorption-reagent (**698**), filling the bulb (*c*, fig. 97) completely, but allowing only a small quantity of the liquid to remain in (*d*). The liquid is introduced, by pouring it into the wide tube above (*d*). The liquid should be drawn nearly to the top of the porcelain scale by applying suction to the capillary-tube (*a*), and before a measurement is taken the liquid should always be brought again to the same level.

When the pipette is not in use, the reagent is protected from the air by closing the wide tube with a cork, and the capillary-tube is closed with a piece of rubber tube which is stopped with a short piece of glass rod.

Process of Absorption.—Next proceed to absorb the constituents successively from the gaseous mixture which is contained in the measuring-tube. Connect the measuring-tube with the absorption-pipette, by means of the bent capillary-tube, squeezing the end of the rubber tube to exclude air. Raise the pressure-tube slightly, and then open both pinch-cocks. The gas will pass over from the measuring-tube

to the absorption-pipette. As soon as the gas has passed completely into the bulb, close both pinch-cocks, gently shake the contents of the bulb, and allow the gas to stand in contact with the absorbent for five minutes.

Then transfer the gas back to the measuring-tube again, by lowering the pressure-tube and opening the clamps. As soon as the gas has passed over, close the pinch-cocks.

Now raise the pressure-tube until the water in both tubes is at the same level, after allowing an interval of two minutes for the water to drain from the side of the tube, and read off the volume of the gas.

Transfer the gas again to the pipette, and shake it gently with the reagent for a minute; then measure its volume once more in the burette. If the volume is the same as before, the absorption is complete; the volume of the gas is therefore noted down, and the next absorption is proceeded with. If a further decrease of volume occurs, the absorption must be repeated. More than two absorptions are rarely necessary to remove any one gaseous constituent completely.

Subsequent absorptions are effected in precisely the way which has been just described, each gas being absorbed by the reagent which is specified in paragraph **698**. A separate pipette should be kept for each reagent.

697. The Winkler Burette.—Another form of burette, known as the Winkler-burette, must be employed for the analysis of gaseous mixtures which contain a constituent soluble in water.

It is of the same shape as the Hempel-burette, but the top of the measuring-tube is supplied with a stopcock, and the bottom with a three-way cock similar to that shown in fig. 100 (p. 452). By this arrangement the measuring-tube can be cut off from the water in the pressure-tube, and a stream of gas can be passed through the stopcock into the measuring-tube, and out into the air by means of the three-way cock.

The measuring-tube is of 100 c.c. capacity, and is graduated in fifths of a c.c.

Before the measuring-tube is used, it must be dried. This is most rapidly effected by rinsing it out with alcohol, then with ether, and finally blowing air through it from bellows.

The measuring-tube is filled with the gas to be examined, either by passing a continuous current of the gas through it, until all the

air has been displaced, or by filling the tube with mercury, and letting the gas displace the mercury. The stopcocks are now closed, and 100 c.c. of the gas, under atmospheric temperature and pressure, are obtained for analysis.

The tube can then be connected with a Hempel-pipette. The other manipulations with this burette are the same as with the Hempel-burette.

698. Reagents for absorption of Gases in the Hempel Pipette.—The following directions serve for the preparation of absorption-reagents of suitable strength for gas-analysis.

(a). **Potassium Hydrate Solution.**—A solution of 1·2 specific gravity is made by dissolving 120 grams of ordinary potassium hydrate in 500 c.c. of water.

This solution is used for absorbing carbon dioxide, and acid gases generally.

(b). **Alkaline Pyrogallate Solution.**—Dissolve 20 grams of pyrogallic acid in 200 c.c. of the potassium hydrate solution (a). The solution should be kept in a pipette of the simple form (694), the openings of which are carefully closed from the air when the pipette is not in use. Or the pipette may be provided with the two guard-bulbs (*m*, *n*) shown in fig. 98.

This solution is used for absorbing oxygen.

Caution.—During the absorption of oxygen by the alkaline pyrogallate solution, carbon monoxide gas is evolved in small quantity. If the proportion of oxygen in the mixture is small, the error from this cause is inappreciable. If, however, the gas consists mainly of oxygen, a serious source of error is thus introduced.

The error may be rectified or prevented by one of the following methods of procedure, the selection between them depending upon whether carbon monoxide was originally present in the gas which is being analysed.

(1). If the sample of gas was known to be free from carbon monoxide, the carbon monoxide which is produced by the pyrogallate can be removed by absorption with cuprous chloride solution (c), and the true volume of oxygen absorbed is thus ascertained.

(2). If the sample of gas originally contained carbon monoxide, it is diluted with a known volume of pure hydrogen or nitrogen, or of air which has been freed from carbon dioxide, and contains a known proportion of oxygen. The gas must be thus diluted until the pro-

portion of oxygen present is less than twenty-five per cent. of the whole mixture. The absorption with pyrogallate can then be proceeded with in the usual way.

Instead of absorbing the oxygen by means of pyrogallate, it may be removed by combustion with hydrogen (**715**).

(c). **Cuprous Chloride Solution.**—Pass sulphur dioxide into a solution of 1 part of sodium chloride and 2 parts of crystallised copper sulphate. Wash the precipitate of cuprous chloride first with solution of sulphurous acid, and then with glacial acetic acid. Then press it between filter-paper and dry it at 100° C.

The salt may be used either in ammoniacal or in acid solution. The acid solution is to be preferred unless the combustion of hydrogen by palladinised asbestos (**709**) is to follow. The solution is used for absorbing carbon monoxide.

(1) *Ammoniacal Solution* is prepared by dissolving 15 grams of cuprous chloride in about 100 c.c. of water, in a flask of about 250 c.c. capacity. Ammonia gas is passed into the liquid until all the cuprous chloride is dissolved and the solution assumes a pale blue colour. The liquid is then diluted to 200 c.c. This solution can absorb about 6 c.c. of carbon monoxide. During the preparation and storage of the solution, contact with air must be avoided as much as possible.

(2) *Acid Solution* is prepared by dissolving 27 grams of cuprous chloride in 200 c.c. of hydrochloric acid of 1·124 specific gravity.

(d). **Alcohol.**—Rectified spirit is used for absorbing the vapours of hydrocarbons.

(e). **Iodine solution.**—Deci-normal solution of iodine in potassium iodide solution is used for absorbing sulphur dioxide. *Potassium dichromate* in saturated solution may be used for the same purpose.

(f). **Ferrous sulphate** in cold saturated solution is used for absorbing nitric oxide. *Potassium Permanganate* solution acidified with sulphuric acid may be used for the same purpose.

(g). **Bromine-water**, made by shaking bromine with water, until the water is saturated, is used for absorbing the olefine hydrocarbons. *Fuming Sulphuric Acid* serves the same purpose.

(h). **Fuming Nitric acid** may be used for absorbing the vapour of benzenes.

Collection of Gas for Analysis.

699. The Method of Collecting a Sample of Gas will vary according to the conditions under which it has to be taken, conveyed, and stored. If it is collected in the laboratory, it is generally passed direct into the Hempel-burette (**696**) or the Winkler-burette (**697**). If a larger quantity has to be stored, it is collected in a glass gas-holder. If the gas must not come into contact with water, it is passed up into a tube filled with mercury, which is then closed by inverting its open end in a vessel of mercury.

A sample of gas which has to be collected away from the laboratory may occasionally be taken and safely stored as is directed above. The sample is, however, usually sealed in a glass tube, which is made by drawing off a piece of broad glass tubing near each end to capillary bore, leaving the intermediate tube with a capacity of from 50 to 100 c.c.

The air is displaced from the tube by passing through it a stream of the gas, either by its own pressure or by suction applied by an aspirator (**58, 141**). A free current of the gas should pass through the tube for at least fifteen minutes. The two capillaries are then sealed by the blowpipe.

If the supply of gas, which is available, is small, the tube is prepared as above, and the air is removed from it by a good air-pump. The tube is then sealed, and one end is opened in the gas to be collected; the tube is then again sealed.

When the sample is to be withdrawn into the Hempel-burette, a file-mark is made near each end of the sample-tube. One end is attached by the rubber joint (*a*, fig. 99, p. 438)

to the Hempel-burette, while the other end is immersed in a vessel of water or other suitable liquid. Both the ends are then broken off, and the gas is drawn over into the burette in the usual way by lowering the pressure-tube (*d*).

Estimation of Gases by Absorption in the Hempel Apparatus.

The method of estimating the constituents of several ordinary gaseous mixtures, by means of the Hempel-apparatus, is given below. The general procedure and manipulation are described in par. 696.

700. Estimation of Carbon Dioxide in Furnace Gases.—Employ a simple absorption-pipette (694) containing the solution of potassium hydrate (698, a). A more exact method of estimating small proportions of carbon dioxide is described in paragraph 718.

701. Estimation of Oxygen in Atmospheric Air.—Employ the absorption-pipette with a strong solution of alkaline pyrogallate (698, b).

702. Estimation of Carbon Dioxide, Oxygen, and Nitrogen in a Furnace Gas.—Absorb the gases in the following order, by the reagents specified.

(1) Carbon dioxide, by potassium hydrate solution (698, a).
(2) Oxygen, by alkaline pyrogallate solution (698, b).
(3) Measure the residual nitrogen.

703. Estimation of Carbon Dioxide, Oxygen, Carbon Monoxide, and Nitrogen in a Furnace Gas.—Absorb the gases in the following order, by the reagents specified.

(1) Carbon dioxide, by potassium hydrate solution (698, a).
(2) Oxygen, by alkaline pyrogallate solution (698, b).
(3) Carbon monoxide, by freshly prepared cuprous chloride in acid solution (698, c).
(4) Measure the residual nitrogen.

704. Estimation of Carbon dioxide, Olefines, Benzene, Oxygen, and Carbon monoxide in Coal gas, Generator gas, and Similar Mixtures.—Absorb the gases in the following order, by the reagents specified, using a Hempel-burette containing water saturated with the gas which is to be analysed.

(1) Carbon dioxide, by potassium hydrate solution (**698, a**).
(2) Olefines, by saturated bromine-water; subsequently removing the bromine-vapour by means of potassium hydrate solution in a separate pipette (see *Note*).
(3) Benzene, by fuming nitric acid; subsequently removing the nitrogen oxides by means of the potassium hydrate pipette (see *Note*).
(4) Oxygen, by alkaline pyrogallate solution (**698, b**).
(5) Carbon monoxide, by freshly made cuprous chloride dissolved in ammonia solution (**698, c**).
(6) The residual gas is transferred to a Hempel-pipette charged with water, and hydrogen and methane are estimated as is directed in paragraph **710**; nitrogen will then remain as a residue.

Note.—In the above process, the separate absorption of the olefine hydrocarbons and benzene by bromine-water and by nitric acid respectively is not very satisfactory.

An alternative method is to absorb these substances simultaneously by fuming sulphuric acid, followed by caustic potash solution.

705. By Employing the Winkler Burette (697) or the Lunge Nitrometer (718) the following gases, which are soluble in water, can be estimated by means of the absorbents specified in each case.

Ammonia by dilute sulphuric acid.

Nitrogen peroxide by concentrated sulphuric acid, or by a solution of potassium permanganate acidified with sulphuric acid.

Nitric oxide by a concentrated solution of ferrous sulphate, or by potassium permanganate acidified with sulphuric acid.

Nitrous oxide by alcohol.
Chlorine by solution of potassium hydrate (698, a).
Hydrochloric acid by the same.
Hydrogen sulphide by the same.
Sulphur dioxide by the same, by iodine solution (698, e), or by saturated solution of potassium dichromate.

Estimation of Gases by Combustion in the Hempel Apparatus.

706. Estimation of Hydrogen by Combustion in Air, aided by Palladinised Asbestos.—The hydrogen is mixed with air, and is passed through a glass tube of 1 millimetre bore, which contains a fibre of asbestos covered with finely-divided palladium. The asbestos is gently heated while the hydrogen and air is being passed over it. The hydrogen combines with the oxygen of the air to form water. From the contraction in volume which occurs, the volume of hydrogen which was originally present is calculated. A narrow tube made of palladium may replace the glass tube containing palladinised asbestos.

Hydrogen gas is burnt readily in this way; carbon monoxide is burnt more slowly than hydrogen. Methane is not burnt at all.

707. Preparation of the Palladinised Asbestos.—Dissolve 1 gram of palladium in aqua-regia, and evaporate the solution to dryness on the water-bath to remove free acid. Dissolve the residue in a small quantity of water, and add about 5 c.c. of a saturated solution of sodium formate. Then add sodium carbonate solution, until the reaction of the liquid is strongly alkaline.

Introduce into this liquid about 1 gram of soft, long-fibred asbestos; this should absorb the whole of the solution. Remove the asbestos, and heat it gently at first; finally heat it on the water-bath until it is perfectly dry; then soak the fibres in a little water, remove them to a funnel, and wash out the soluble salts.

The palladinised asbestos thus prepared is of a grey colour, and contains about 50 per cent. of palladium. It will cause a mixture of hydrogen and oxygen to combine at the ordinary temperature of the air, but this result is more rapidly attained if the fibre is heated.

708. Preparation of the Capillary Combustion-tube.—Cut off a piece 8 inches in length from a length of hard glass, thick-walled tube, 1 millimetre in bore. Lay a few loose palladinised-asbestos fibres (**707**), about 1½ inches in length, side by side on smooth filter-paper. Moisten them with a drop or two of water, and twist them into a thread about as thick as stout sewing-cotton. Take up this thread with the forceps, and push it down the capillary-tube, which is meanwhile held vertically. Now fill the tube with water, and bring the asbestos thread into the middle of the tube by shaking the tube. Then dry the tube, and bend down its ends at right angles. It is now ready to take the place of the ordinary capillary-tube (*c*, fig. 99, p. 438).

709. *The Process of Estimation of Hydrogen.*—Read off the volume of the hydrogen gas, which should not exceed 25 c.c. Lower the pressure-tube of the burette, and allow about 75 c.c. of air to enter the measuring-tube. Read the total volume of gas accurately, after levelling the water. Now interpose the capillary combustion-tube between the burette and a simple absorption-pipette (**694**) which is charged with water only.

Gently heat the middle of the capillary-tube (**708**) short of redness by a small flat gas-flame, or by the flame of a spirit-lamp. Then cause the gaseous mixture to pass through the capillary-tube from the measuring-tube into the pipette, by raising the pressure-tube. The end of the asbestos thread will usually glow as soon as the gas reaches it. Do not remove the source of heat, else water may condense and break the tube.

As soon as the gas has passed completely over, draw it back again through the heated capillary into the measuring-tube. Then repeat the passage backwards and forwards over the heated asbestos. In the case of a readily combustible gas like hydrogen, the combustion should now be complete. Read off the volume accurately, and note if it becomes reduced by one more passage over the hot asbestos. The combustion must be continued, until no decrease of volume is noticed after the last passage over the heated asbestos.

The residual gas is then measured, and the contraction of

volume which has been caused by the combustion is found. From this the quantity of gas which has been burnt can be calculated directly in the case of hydrogen.

It is well to obtain some experience by performing several estimations with known volumes of hydrogen and air, before making an estimation of an unknown volume of hydrogen.

Example.—In a particular estimation, the following numbers were obtained.

The volume of hydrogen employed = 22·8 c.c.
The total volume of hydrogen + air = 98·0 c.c.
Hence the volume of air added = 98·0 − 22·8 = 75·2 c.c.

Assuming the percentage volume of oxygen in air to be 21, the volume of oxygen introduced = 15·8. By theory 22·8 c.c. of hydrogen would require 11·4 c.c. of oxygen for their complete combustion; hence there is an excess of 4·4 c.c. of oxygen, if the gas taken is pure hydrogen.

The volume of residual gas after combustion = 64·0 c.c.
Therefore the volume of gas which has disappeared during the combustion = 98·0 − 64·0 = 34 c.c.

Hence the volume of hydrogen $= \frac{34 \times 2}{3} = 22{\cdot}66$.

710. Estimation of Hydrogen, Methane, and Nitrogen.

In the analysis of coal-gas and similar mixtures the gases mentioned in par. **704** are first removed by absorption.

Two methods may then be adopted. Either (1) the hydrogen may be *first* estimated by being burnt (**709**), and the methane may then be fired with air or with oxygen; or (2) the hydrogen and methane may be fired *simultaneously* with air or oxygen. In either case the nitrogen will be measured by difference.

(1) The Hempel apparatus is charged with water as usual, and the gas, or an aliquot portion of it, is then mixed with air, and the hydrogen is estimated as is described above (**709**). The gaseous mixture can now only contain the methane and nitrogen, together with a known volume of nitrogen and oxygen from the air added. The methane

and nitrogen in this mixture are estimated in the following way.

About 20 c.c. of the gas is mixed with more than the volume of air or oxygen required for its complete combustion, which is also carefully measured: the mixture is then fired.

Precautions.—Bunsen states that the proportion of combustible to incombustible gas must be within the limits of from 26 to 64 per cent., else nitrogen oxides may be formed. If the proportions are less than these, the mixture refuses to burn. No general rule can be given as to the exact proportions to employ; but the explosion should be observed, and must be sufficiently rapid not to be followed in its progress down the bulb by the eye. If the mixture contains an insufficient quantity of combustible gas to explode when it is mixed with oxygen or with air, a measured quantity of pure hydrogen must be added.

The mixture is fired by the spark from an induction-coil in a special form of Hempel Explosion-burette containing mercury instead of water. The decrease of volume caused by the firing is noted, and the further diminution of volume caused by the absorption of the carbon dioxide produced is also noted. The volume of methane originally present in the mixture is equal to the volume of carbon dioxide absorbed, as is seen from the equation:—

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

The volume of nitrogen in the original mixture is found by subtracting the volumes of hydrogen and methane from the volume of the original mixture.

(2) About 15 c.c. of the mixture of hydrogen, methane, and nitrogen is made up to 100 c.c. by mixture with air: or about 30 c.c. of the mixture is made up to 75 c.c. by addition of oxygen (see *Precautions*, above).

The mixture is fired as is directed above (1), the contraction of volume caused by firing is noted, and the further contraction caused by absorbing the carbon dioxide with potassium hydrate solution is also noted. The volumes of hydrogen and of methane are then calculated as follows:—

If x = contraction of volume on firing, and
y = contraction of volume by absorption with potash,

$$\text{Then vol. of H} = \frac{2}{3}(x - 2y)$$

$$\text{and vol. of } CH_4 = y.$$

The above statement depends upon the facts that the contraction of volume on firing is due to the combination of free and combined hydrogen to form water, and that the CH_4 forms its own volume of carbon dioxide.

711. Example of Coal-Gas Analysis.—The sample was collected in a Hempel-burette, containing water, which had been previously saturated with coal-gas by passing the gas through it. The original volume of gas was 99 c.c. The gas was treated successively with the following reagents with the results stated.

(1). Potassium hydrate gave no absorption, hence carbon dioxide was absent.

(2). Alkaline pyrogallate solution:—

Before absorption = 99·0 c.c.
After absorption = 98·8 c.c.

Volume of oxygen = 0·2 c.c.

$$\therefore \text{ Percentage of oxygen} = 0{\cdot}2 \times \frac{100}{99} = \underline{0{\cdot}2}$$

(3). Nordhausen sulphuric acid, followed by potassium hydrate solution:—

Before absorption = 98·8 c.c.
After absorption = 93·5 c.c.

Volume of olefines and benzene = 5·3 c.c.

$$\therefore \text{ Percentage of olefines and benzene} = 5{\cdot}3 \times \frac{100}{99} = \underline{5{\cdot}2}$$

(4). Cuprous chloride solution:—

Before absorption = 93·5 c.c.
After absorption = 87·0 c.c.

Volume of carbon monoxide = 6·5 c.c.

$$\therefore \text{ Percentage of carbon monoxide} = 6{\cdot}5 \times \frac{100}{99} = \underline{6{\cdot}5}$$

(5). The residual 87 c.c. of gas containing methane, hydrogen, and nitrogen were transferred to the carbon monoxide pipette: the water in the burette was exchanged for water saturated with air.

30·8 c.c. of the gas was then mixed with oxygen in the burette

until the total volume was 75·2 c.c. This mixture was fired with the spark of the induction coil, and the residue was exposed to absorption by potassium hydrate solution. The volumes read were as follows:—

Before firing = 75·2 c.c.
After firing = 25·9 c.c.

Total contraction = 49·3 c.c.

Before absorption = 25·9 c.c.
After absorption = 13·9 c.c.

Carbon dioxide from methane = 12·0 c.c.

Hence the volume of methane = 12·0 c.c.

$$\therefore \text{ Percentage of methane} = 12 \times \frac{87}{30{\cdot}8} \times \frac{100}{99} = 34{\cdot}2$$

$$\text{And the volume of hydrogen} = \frac{2(49{\cdot}3 - 2 \times 12}{3} = \frac{2 \times 25{\cdot}3}{3} = 16{\cdot}9$$

$$\therefore \text{ Percentage of hydrogen} = 16{\cdot}9 \times \frac{87}{30{\cdot}8} \times \frac{100}{99} = 48{\cdot}2$$

For Statement of Results, see Appendix (**772**).

712. Estimation of Carbon Monoxide by Combustion.—The above process for estimating hydrogen (**709**) is also applicable to the estimation of carbon monoxide in a furnace-gas, if the carbon dioxide present in the mixture has been first removed by absorption. From the equation,

$$\underset{\text{2 vols.}}{CO} + \underset{\text{1 vol.}}{O} = \underset{\text{2 vols.}}{CO_2},$$

it will be seen that the original volume of CO is equal to double the contraction caused by its combustion; or to two-thirds of the total contraction caused by the combustion, followed by the absorption of the resulting carbon dioxide by potassium hydrate solution.

When carbon monoxide is to be estimated in the presence of hydrogen, it is necessary to note also the loss of volume which is afterwards caused by the absorption of the carbon dioxide produced, in order to calculate the volume of each of the combustible gases.

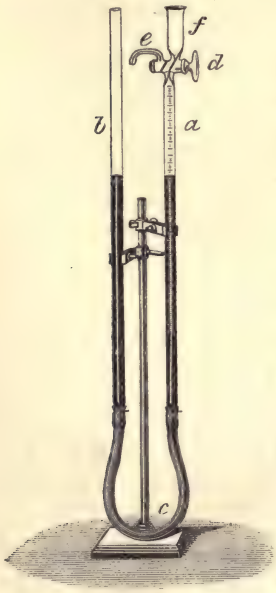
713. Estimation of Oxygen by Combustion.—The proportion of oxygen present in the atmosphere may also be estimated by the process described above for hydrogen (**709**). A known volume of hydrogen in excess is added to the air, and the decrease of volume caused by its combustion is noted. The volume of oxygen is equal to one-third of this decrease.

THE LUNGE NITROMETER.

714. The Lunge Nitrometer (fig. 100) is so called because it was originally devised for the analysis of "nitrous vitriol." It can be used for many analytical processes which involve the measurement of a gas.

Like the Hempel Burette, it consists of two tubes, the measuring-tube and the pressure-tube. The measuring-tube (*a*) in figure 100 holds 50 c.c., and is graduated into fifths of a c.c.: it is calibrated according to the directions in par. **690**. The measuring-tube is connected by means of *thick-walled* rubber tubing with the pressure-tube (*b*), which is not graduated. The apparatus is usually charged with mercury; but water, glycerine, or oil may be used for special purposes instead of mercury.

FIG. 100.



To the top of the measuring-tube (*a*) is fitted Greiner and Friedrich's patent stopcock (*d*), in connection with which is a cup (*f*), and a strong capillary-tube (*e*).

In the figure the stopcock is so set as to open communication between the measuring-tube and the cup. If the stopcock is turned half round, communication will be made between the capillary-tube (*e*) and the measuring-tube. When the stopcock is turned one-quarter round, communication between the air, the tube (*a*) and the cup (*f*) is cut off.

It will be seen, therefore, that this stopcock renders it

possible to draw a gas into the measuring-tube through the capillary inlet (*e*). The gas can then be exposed to a liquid reagent by pouring the reagent into the cup (*f*), and then putting the cup (*f*) into communication with the measuring-tube (*a*) and drawing the liquid into the measuring-tube by lowering the pressure-tube (*b*). The entrance of air is prevented by turning the stopcock one-quarter round, as soon as all the liquid has entered.

715. Another Form of the Nitrometer is used for measuring larger quantities of gas. For this purpose a bulb is blown in the measuring-tube (*a*) immediately under the stopcock. The bulb has a capacity of about 100 c.c., and the first graduation on the tube below the bulb is for 100 c.c. ; the graduations are continued down the tube until 140 c.c. is reached. A bulb is also blown upon the bottom of the pressure-tube (*b*), which is of sufficient capacity to hold the mercury which is required for the measuring-tube.

According to the volume of gas to be dealt with, the ordinary form or the more capacious form of the nitrometer is used.

A number of applications of the Lunge-nitrometer are described below.

Estimation of the Amount of Nitrogen Oxides in Nitrous Vitriol.

716. Remove the stopcock (*d*) from the measuring-tube of the nitrometer (fig. 100), and carefully dry both the surface of the stopcock and of the tube into which it fits. Then lightly smear some resin cerate, vaseline, or lard over the surface of the stopcock ; insert the stopcock, and turn it until the cup (*f*) is in communication with the measuring-tube (*a*).

Now fill in mercury, until, on raising the pressure-tube the mercury fills the measuring-tube (*a*) just entering the stopcock, and reaches a level of about 2 inches in the pres-

sure-tube (*b*). Take care to remove all air-bubbles from the measuring-tube.

Then close the stopcock, and lower the pressure-tube until the level of mercury in it is considerably below that in the measuring-tube (*a*). If the apparatus is air-tight and has been freed from air-bubbles, no bubble of air will be visible at the top of the mercury column in the measuring-tube (*a*), after several minutes. Then bring the surfaces of the columns of mercury in both tubes to the same level by raising the pressure-tube (*b*).

Now pour into the cup (*f*) a quantity of the nitrous vitriol, varying from 0·5 to 5 c.c. according to the quantity of nitrogen oxide which it is believed to contain.

Note.—If any SO_2 is present in the nitrous vitriol, it must be oxidised by adding a *small quantity* of powdered potassium permanganate before the acid is introduced into the nitrometer.

Cautiously open the stopcock, and allow all the acid, except a small drop, to run into the measuring-tube (*a*). Then pour into the cup 3 c.c. of strong sulphuric acid, free from nitrous compounds, and allow this to run into the measuring-tube (*a*). Repeat this operation with 3 c.c. more of the acid, taking care that no air-bubbles enter the tube.

Now grasp the measuring-tube in the hand, and unclamp it. Start the evolution of gas by lowering the tube several times almost to the horizontal position, and suddenly raising it again to an upright position. Then shake up the mercury with the acid until no more gas is given off.

Now clamp the tubes (*a*, *b*) at such relative heights that the gas in the measuring-tube is approximately under atmospheric pressure. This may be effected by assuming that 6·5 mm. of the strong acid in the measuring-tube balance 1 mm. of mercury in the pressure-tube. Allow the apparatus to stand until its contents have gained the temperature of the air.

The levels of the tubes are now once more adjusted, if necessary. A little strong acid is then poured into the cup (*f*): and the stopcock (*d*) is cautiously turned, so as to

place the cup and measuring-tube for a moment in communication with one another. It is then easily seen whether the acid in the cup tends to enter the measuring-tube, or to be expelled; and the level of the pressure-tube can be adjusted accordingly, until the gas is proved by slightly opening the stopcock to be exactly under atmospheric pressure.

The measuring-tube should always be grasped by the cup (*f*) during the above final adjustments, so as to avoid heating and expanding the gas, by touching the graduated part of the tube with the hand.

The volume of the gas is then read off, and the atmospheric temperature and pressure are noted down at the same time. In accurate work another reading should be taken in half an hour, and if this agrees with the former one the gas had previously attained the atmospheric temperature.

Each c.c. of nitric oxide at 0° and 760 mm. (**685**, 1) represents 1·343 milligrams of this gas. This is equivalent to 0·627 milligrams of nitrogen, to 1·701 milligrams of nitrogen trioxide, and to 2·830 milligrams of nitric acid.

After the reading of the volume has been taken, lower the measuring-tube (*a*), lest air should enter when the stopcock is opened. Then open the stopcock, and raise the pressure-tube (*b*), so as to expel both the gas and the acid. Then allow the acid thus collected in the cup to flow out into a beaker through the capillary (*e*), removing the last drop of acid from the cup by means of filter-paper.

Estimation of an Alkaline nitrate by the Lunge Nitrometer.

717. The above process (**716**) is easily adapted to the estimation of commercial potassium or sodium nitrate. A quantity of the nitrate, which will evolve rather more than 100 c.c. of nitric oxide gas, is weighed, and is introduced

into the larger form of the nitrometer (**715**) as is directed below.

For practice in the process, weigh out 0·35 gram of finely-powdered sodium nitrate. Place this powder in the cup (*f*) of the nitrometer, and add about half a c.c. of water. As soon as the nitrate is dissolved, draw the solution into the measuring-tube. Pour half a c.c. of water into the cup, and draw this also into the measuring-tube.

Finally introduce 15 c.c. of strong sulphuric acid, and proceed to make the estimation, as is described in paragraph **716**. The apparatus should stand for two hours, before the reading of the volume is taken, in order that the gas may gain the atmospheric temperature; and another reading taken half an hour later should correspond with the first.

After correcting the volume of the gas for pressure and temperature (**685**, 1), each c.c. represents 3·805 milligrams of sodium nitrate and 4·522 milligrams of potassium nitrate.

Gas-analysis by the Lunge Nitrometer.

718. By employing the Lunge-nitrometer (**714**), and the Hempel-pipettes (**694**), gases which are soluble in water can be estimated. Instead of the ordinary Hempel-pipettes, similar pipettes of smaller size, and partially filled with mercury, may be used.

All the gases mentioned in paragraph **705**, except chlorine, may be estimated in this way by means of the nitrometer.

In certain cases the absorption may be effected in the nitrometer itself. For this purpose the absorbent liquid is drawn from the cup into a measured volume of the gas, contained in the measuring-tube. The tube is then shaken, and the volume of the residual gas is read off, as has been already described (**716**).

Analysis of Gases dissolved in Water or other Liquids.

719. For the purpose of estimating dissolved gases, connect a flask with the capillary-tube (*e*) of the Lunge-nitrometer (**714**) by means of a short piece of rubber tubing. One end of this tubing is fitted upon the capillary-tube (*e*), the other is attached to a short piece of glass tube which passes just through a cork fitting the neck of the flask.

Now charge the nitrometer with mercury (**716**), and fill the flask with the liquid containing the gas. Connect the capillary (*e*) with the measuring-tube (*a*), and press down the cork into the neck of the flask. The air from the connecting-tube is thus transferred to the measuring-tube, and the liquid will fill the capillary-tube. Shift the position of the stopcock, and expel the air from the measuring-tube through the cup (*f*) by raising the mercury level.

Again connect the flask with the tube (*a*), and heat the liquid in the flask until all the dissolved gas is expelled. Collect the gas in the measuring-tube, by lowering the pressure-tube. Allow the gas to cool, and measure it. Then proceed to analyse the gas by submitting it to the necessary absorbents (**698**).

A more accurate method of collecting the gases dissolved in water, by means of special apparatus, is described by Dr Truman in the *Journal of the Chemical Society*, Jan. 1894.

Estimation of Substances, which evolve a Definite Amount of Gas when they are Decomposed.

720. For the estimations described in paragraphs **720**–**723**, either the Lunge-nitrometer or the apparatus described in paragraphs **725**, **728** may be used.

The Lunge apparatus is usually filled with mercury, but other liquids may be substituted in special estimations. Thus in

testing sweet spirit of nitre, by measuring the amount of nitric oxide gas evolved when the spirit is treated with a solution of potassium iodide and sulphuric acid, a solution of salt is used instead of mercury.

In some cases the decomposition of the substance may be effected in the nitrometer itself, as is described under the estimation of sodium nitrate (**717**).

When the substance is decomposed in a flask connected with the nitrometer (**719**), and the amount of air displaced by the gas is measured, mercury should always be employed. An illustration is furnished by the estimation of the amount of carbon dioxide evolved from a carbonate by treatment with an acid. The bottle, containing a separate tube, described in paragraph **725**, will serve for the decomposition of the body; but a flask which has an inside tube fused in a vertical position upon the bottom, will be found more convenient, since the risk of breaking the tube is thus avoided.

If mercury is used in the nitrometer, the flask may be connected, by means of a tube passing through the cork and a *short* piece of rubber tubing, with the capillary-tube (*e*) of the nitrometer.

In calculating the percentage weight of the substance from the volume of gas read off, it will be necessary to calculate the volume of the dry gas at normal temperature and pressure (**685**, 2), and then to calculate its weight.

721. Estimation of Ammonium Salts and of Urea in Urine.—The Lunge-apparatus, or that described in paragraph **728**, may be used in the estimation of urea and of ammonium salts.

About 0·25 gram of the substance, if it is solid, is accurately weighed out, and is introduced into the decomposing flask (A, fig. 101, p. 462). 10 c.c. of the sodium hypobromite solution (**727**) are then introduced into the inner tube. The cork is now fitted into the flask, and the flask is connected with the capillary-tube (*e*) of the nitrometer, as has been already described, the nitrometer being charged with mercury.

The tap of the nitrometer is then turned, so as to bring the flask into communication with the measuring-tube, and the flask is turned on its side, and shaken until no more gas is given off. The mercury levels are now adjusted roughly, and the whole apparatus is allowed to stand for fifteen minutes. The levels are then accurately adjusted, and the volume of the gas, and the atmospheric temperature and pressure, are read. The volume of gas is then corrected for tension of water vapour, and for temperature and pressure (685, 2).

Ammonia evolves, under the above conditions, 97·5 per cent. of its nitrogen, and urea 92 per cent. Each c.c. of nitrogen evolved, when corrected for temperature, pressure, and moisture (685, 2), accordingly corresponds to 0·001562 gram of ammonia, and to 0·002952 gram of urea.

Each c.c. of N may be taken as representing 0·002687 gram of urea, on the assumption that the urea evolves all its nitrogen; this assumption is only true when much sugar is present (726).

722. Estimation of Substances, which evolve Carbon Dioxide, when they are Decomposed.—The above apparatus (720) can also be used for estimating the carbon dioxide evolved from carbonates, such as the commercial alkaline carbonates and bicarbonates, limestone and bone-charcoal. The apparatus also serves for the valuation of manganese-ores by means of oxalic acid (346), and for estimating oxalates by means of manganese dioxide (150).

The amount of carbon dioxide evolved falls below that contained in the substance, owing to the solubility of the gas in the acid; but it is stated that the addition of 7 per cent. to the observed volume corrects this deficiency, if 10 c.c. of hydrochloric, of 1·12 specific gravity, are used in the estimation.

723. Estimations by Treatment with Hydrogen Peroxide and Measurement of the Oxygen evolved.—When certain bodies, which contain "active oxygen," are brought into contact with hydrogen per-

oxide, the active oxygen of both substances is liberated as oxygen gas. The measurement of the volume of oxygen evolved serves to indicate the amount of the substance present. The following bodies may be estimated in this way.

(a). **Hydrogen Peroxide** may be mixed with excess of an acid solution of potassium permanganate. Two c.c. of hydrogen peroxide are poured into the decomposition flask, and an excess of a solution of potassium permanganate in dilute sulphuric acid is poured into the inner tube. The following reaction occurs, when the liquids are mixed :—

$$K_2Mn_2O_8 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Half the volume of oxygen which is liberated is accordingly yielded by the hydrogen peroxide.

(b). **Potassium Permanganate.**—The process is the converse of the preceding one (a) ; excess of H_2O_2 being allowed to act upon a weighed quantity of the permanganate in solution.

(c). **Manganese Ores.**—Any carbonate present in the ore is first decomposed by means of dilute H_2SO_4, excess of H_2O_2 is then added, and the evolved oxygen is measured :—

$$MnO_2 + H_2SO_4 + H_2O_2 = O_2 + MnSO_4 + 2H_2O.$$

(d). **Bleaching-powder.**—The bleaching-powder solution is treated with H_2O_2, as is described above. Half the total volume of oxygen evolved is liberated by the bleaching-powder, and each c.c. of oxygen which is liberated by the bleaching-powder corresponds to 0·006341 gram of available chlorine.

SPECIAL FORMS OF GAS-APPARATUS.

Estimation of Carbon Dioxide in a Carbonate by Volume.

724. The carbon dioxide in a carbonate may be estimated by liberating the gas by the action of an acid, and measuring its volume. From this result the weight of the carbon dioxide can be calculated ; the weight of the carbonate itself

may then be calculated, if it is of known and definite composition.

Most forms of gas-apparatus may be used for measuring the evolved gas, and the results obtained will be accurate, if the necessary precautions are taken. The Lunge-nitrometer (**714**), or the Hempel apparatus (**692**), may be conveniently employed; but a special form of apparatus is described below which is rapid and simple in use.

725. Scheibler's Apparatus was originally designed for estimating the amount of calcium carbonate present in the bone-black which is used in sugar-refining.

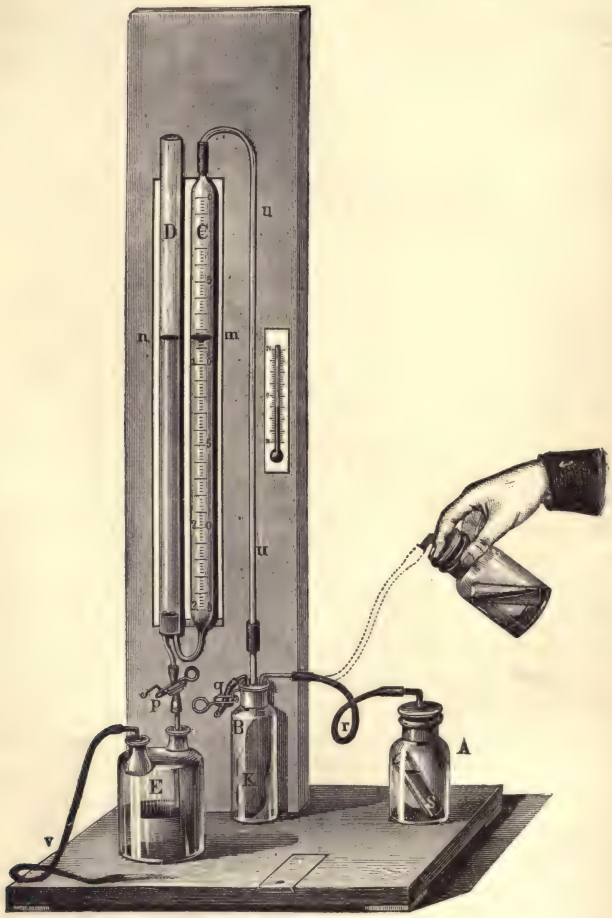
Description of the Apparatus.—The apparatus is shown in fig. 101. The vessel in which the weighed quantity of carbonate is decomposed is seen at A. This vessel contains a glass or gutta-percha tube of about 12 c.c. capacity, in which the acid required for the decomposition is placed. The vessel (A) is closed by a sound perforated rubber cork, into the perforation in which a short bent glass tube is fitted. This is connected by means of rubber tubing (*r*) with the bottle (B), from which the gas displaces air into the measuring-apparatus.

The bottle (B) is closed by a good rubber cork with three perforations. Through one of these passes a bent tube, which is connected air-tight with the vessel (A) by the rubber tube (*r*); into another of these perforations is fitted a long vertical tube (*uu*), which connects B with the measuring-apparatus; and into the third perforation is fitted a short piece of glass tubing, on which is a short piece of rubber tubing, which can be closed by a spring or screw-clamp (*q*); thus serving to open or close the connection of B with the atmosphere at pleasure. A thin rubber toy-balloon, or a collodion balloon, is shown in the bottle, fastened air-tight upon the end of the glass tube connected with the rubber tube (*r*). This balloon can be dispensed with.

The measuring-apparatus consists of two tubes (C), (D), which are firmly fastened to an upright board, forming

part of the stand for the apparatus. These tubes are connected together below; and the tube (D) is also connected

FIG. 101.



with the two-necked bottle (E), which contains water and enables the water-levels in the tubes (C, D) to be adjusted. Water can be run out of the measuring-tubes by opening

the clamp at (*p*); and water can be forced into the tubes by opening (*p*), and blowing with the mouth down the tube (*v*). The measuring-tube C has a capacity of 150 c.c., and is accurately graduated into half c.c.'s.

After fitting up the apparatus, as is shown in the figure, it should be proved to be air-tight by adjusting the water-level in C at a much higher level than that in D, marking the water-levels, and allowing the apparatus to stand for fifteen minutes. If the water-levels remain unchanged, the apparatus is sound.

In making an Estimation, the weighed quantity of finely-powdered carbonate is first introduced into the vessel A, the interior of which must be perfectly dry. The tube, charged with 10 c.c. of hydrochloric acid, of 1·12 specific gravity, is then carefully lowered into the bottle (A). If the balloon (*k*) is used, it is then emptied by suction applied to the tube (*r*). The cork is now inserted into the neck of the bottle (A), and all the connections of the apparatus are made as has been described, and as is shown in the figure.

The clamp at (*q*) being opened, water is then gradually blown up into the measuring-tubes, until it stands exactly at the zero graduation in the tube (C). Great care must be taken not to allow water to pass over into the tube (*u*), or into the bottle (B), as this would involve the necessity of disconnecting and drying this part of the apparatus.

The vessel (A) is then held by its stopper, to prevent heating it by contact with the hand, and is gradually tilted, so as to cause the acid to run slowly out of the tube and to act upon the carbonate. As the liquid in the tube (C) falls, water is constantly allowed to flow out of the measuring-tube by relaxing the clamp (*p*), so as to keep the water at the same level in the tubes (C, D). As soon as the water-level in the tube (C) remains constant for a few seconds, the water in the two tubes is brought to precisely the same level. The volume of gas in the tube (C) is then read off, and the thermometer on the apparatus and the barometer are also

read. These data are sufficient to enable the volume and the weight of CO_2 in the carbonate to be calculated.

It is evident that all risks of warming the apparatus during use, by radiation of heat from the person or from other sources, must be avoided, if the results are to be accurate.

Also if the balloon is dispensed with, the CO_2 must be swept out of the apparatus by an air-current from the bellows after each estimation.

In Calculating the Results, the volume of the gas must be corrected for temperature and pressure, for tension of aqueous vapour (**685**, 2), and for the solubility of CO_2 in the dilute hydrochloric acid. The proportion dissolved may be taken as 7 per cent. of the whole volume of CO_2.

Accordingly, if :—

v = volume of gas measured in c.c.
t = temperature read on thermometer.
p = atmospheric pressure.
w = tension of aqueous vapour at $t°$.

$$\text{The normal volume of } CO_2 = v \times \frac{100}{93} \times \frac{p - w}{760(1 + 0{\cdot}003665t)};$$

$$= \frac{v \times (p - w) \times 1{\cdot}075}{760(1 + 0{\cdot}003665t)}.$$

$$\text{And the weight of } CO_2 = 0{\cdot}0019712 \times \frac{v \times (p - w) \times 1{\cdot}0753}{760(1 + 0{\cdot}003665t)}.$$

Note.—The above corrections of the volume of the CO_2 may be rendered unnecessary, by making an actual experiment with a weighed quantity of pure calcium carbonate, before each series of estimations. From 0·2 to 0·4 gram of powdered calc-spar will be found to be a convenient quantity. This experiment will give the relation between the CO_2 measured and the actual weight of CO_2 or of carbonate, under the conditions of the subsequent estimation. The actual amount of CO_2 can then be calculated from the result of the estimation by a simple proportion statement.

Estimation of Urea by Evolution of Nitrogen.

726. The Estimation of the Percentage of Urea in Urine is frequently required for medical purposes.

The chemical reaction of urea solution, on which the most convenient process of estimation has been founded, is that occurring with an alkaline hypobromite. The result of the reaction is the evolution of 92 per cent. of the nitrogen of the urea. This nitrogen may be collected and measured in any convenient form of gas-apparatus; and the amount of urea, which has evolved it, may be readily calculated.

Certain inaccuracies arise, when the urea is determined by this process in urine instead of in pure urea solution.

Other nitrogenous bodies in the urine besides urea evolve a minute proportion of nitrogen. The amount of nitrogen thus evolved is so small that it may be safely disregarded.

The effect of the presence of glucose in diabetic urine is, however, much more considerable. It tends to increase the proportion of nitrogen which is evolved from the urea by the hypobromite; and if the diabetic urine is mixed with a quantity of cane-sugar ten times as great as that of the urea which it contains, the urea will evolve at least 99 per cent. of its nitrogen. The addition of cane-sugar is recommended when a diabetic urine is being tested, and the larger proportion of nitrogen is then assumed to be evolved.

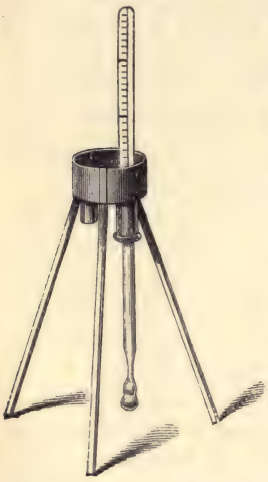
The Lunge apparatus may be used for the process of estimation, as has been already mentioned in paragraph **720**. The following account of the manipulation, which is given in connection with the apparatus devised by Russell and West, can, however, be readily adapted to other forms of apparatus.

727. *The Sodium hypobromite Solution* is prepared by dissolving 100 grams of caustic soda in 250 c.c. of water, and mixing 25 c.c. of this cold solution with 2·5 c.c. of bromine. This mixture will suffice for one determination only, and should be made immediately before the liquid is required

for the estimation. The bromine may be kept sealed in separate tubes in the requisite quantity.

728. The Russell-West Apparatus already referred to is shown in fig. 102. It consists of a little circular metal trough, about $1\frac{3}{4}$ inches deep, and supported by three legs. The decomposition-tube, in which the reaction occurs, is seen beneath the trough, into a tubulure of which it is fitted water-tight by means of a perforated cork. It is a glass tube, about 9 inches long, and about half an inch in internal diameter. Its upper end is somewhat narrowed, and projects above the cork, so as to deliver the escaping gas without loss into the measuring-tube. The lower end consists of a tapering bulb, about 2 inches in length, and constricted at its neck to three-eighths of an inch in internal diameter. The capacity of this bulb should be about 12 c.c. A thin glass rod, about 9 inches in length, is fitted with a narrow ring of rubber tubing round its lower end, so that when it is dropped into the decomposition-tube it closes the constriction above the bulb.

FIG. 102.



The Measuring-tube, in which the nitrogen is collected, is about three-quarters of an inch in internal diameter, and about 40 c.c. in capacity. This tube may be graduated in c.c.'s, but it is usually graduated in such a way that the percentage of urea is read off directly from the graduations. This method of graduation is based on the fact, that 5 c.c. of a 2 per cent. solution of urea evolve 37·1 c.c. of nitrogen, measured at ordinary pressure and temperature, when the solution is treated in the apparatus with hypobromite solution in the

usual way. This volume of nitrogen is accordingly marked as 2 per cent., and the other graduations derived from this will similarly indicate directly percentages of urea.

It may be noted that the increase of the normal volume of the nitrogen at ordinary temperature, which is due to temperature and to the tension of aqueous vapour, almost precisely counterbalances the 8 per cent. deficiency in the volume of the nitrogen which is evolved from the urea.

729. The Process of Estimation.—5 c.c. of urine are allowed to flow from a pipette into the decomposition-tube, and the sides of the tube are rinsed down with distilled water, until the bulb is filled as far as the constriction. The glass rod with rubber end is then placed in the tube, so that it closes the constriction. The decomposition-tube is finally filled with the freshly-prepared hypobromite solution. Water is then poured into the trough until it is half filled: and the measuring-tube is filled with water, closed with the thumb, inverted in the trough, and placed in the little well seen to the left.

The glass rod is now withdrawn, and the measuring-tube is quickly shifted into the other well of the trough, so as to rest upon the cork and cover the opening of the decomposition-tube.

The reaction commences as soon as the urine and the hypobromite solution mingle; and if the bulb is warmed with the flame of a spirit-lamp, the evolution of gas will usually cease entirely in about five minutes. The measuring-tube is then shifted into the well, and the volume of nitrogen is read off as soon as the gas has had time to attain the temperature of the air. The liquid in the decomposition-tube must smell distinctly of the hypobromite, proving that the reagent was present in excess.

730. Excessive Urea and Albumen.—If the urine contains an unusually high percentage of urea, it will be necessary to dilute it with its own volume of water, and to use 5 c.c. of this diluted sample. The result obtained must then be multiplied by 2.

If the proportion of albumen is high, it must be coagulated by adding a few drops of acetic acid to the urine, and heating it: the liquid is then filtered, and the clear filtrate is used for the estimation. If this treatment is omitted, a considerable amount of froth is produced in the measuring-tube, which retards, or renders impossible, the measurement of the nitrogen.

ESTIMATION OF GAS BY ABSORPTION AND TITRATION.

Estimation of Carbon Dioxide in Air by the Pettenkofer Method.

731. Since carbon dioxide is a product both of respiration and of combustion, the estimation of its proportion in the air of closed rooms is of great importance. The result of the estimation enables a judgment to be formed regarding the efficiency of the system of ventilation of a room, and is therefore valuable to engineers and others, who are concerned in the heating and ventilation of buildings.

732. Pettenkofer's Method of determining the Proportion of Carbon Dioxide in Air, depends upon finding the amount of calcium or barium in solution as hydrate, which is precipitated as carbonate from solution, when lime- or baryta-water in excess is well shaken with a known volume of the air.

This is effected by using a known volume of lime-water, the strength of which has been determined by titration with deci-molecular oxalic acid solution. After the lime-water has been exposed to a measured volume of the air, it is again titrated with the acid. The difference between the two volumes of acid required in the titrations gives the weight of oxalic acid which is equivalent to the carbon dioxide absorbed from the air. From this result the weight and the volume of

carbon dioxide which was present in the known volume of air can be calculated.

The following are requisites for this process.

(a). *A Strong Clear Glass Bottle* is selected, from 8 to 10 litres in capacity, and with an unground neck which can be closed air-tight by means of an accurately fitting rubber cork. The exact capacity of the bottle is ascertained by filling it with water to a scratch on the neck, which marks the bottom of the cork: the water is then poured into a measuring-vessel so as to ascertain its volume. The capacity should be written on the bottle with a diamond pencil, or with the point of a sharp file.

The bottle is thoroughly cleansed and rinsed out several times with distilled water. Its interior is then perfectly dried. This is effected either by draining and leaving it open for some time in an inverted position: or, more rapidly, by placing it in a heated oven, and occasionally sucking out the air from the interior by means of a clean dry glass tube, pushed down to the bottom of the bottle, or by blowing out the moist air by bellows. The clean dry rubber cork is then pushed in, until it reaches the mark on the neck.

(b). *A Hand Bellows* with rubber tube on the nozzle is required, by means of which the air from any desired locality can be blown into the bottle for a sufficiently long time, to displace the air in the interior. A volume of air, at least five or six times as great as the capacity of the bottle, should be blown to the bottom of the bottle by the bellows, which are drawing air from the desired position. Fletcher's blowers, or ordinary hand-bellows, may be used. They should be clean and air-tight.

(c). *Saturated Lime-water* is made by repeatedly shaking up freshly-slaked lime with water in a Winchester quart-bottle, which is nearly filled with the water. The solution is rendered clear by subsidence or by filtration. The perfectly clear solution is stored in an accurately stoppered Winchester quart-bottle. Unless alkalis are known to be

absent, a few drops of barium chloride solution are added to the lime-water.

(d). *Standard Oxalic acid Solution* is prepared by dissolving 1·2602 grams of dry pure crystallised oxalic acid in 1 litre of cold distilled water, which has been recently boiled to free it from dissolved CO_2. This dilute solution will not keep unchanged for more than 24 hours. It may either be freshly made as it is required; or a stronger stock solution, containing 126·02 grams per litre, may be diluted one hundredfold immediately before it is used. The dilute solution is a deci-molecular one.

If a standard solution of oxalic acid, containing 2·8636 grams of crystallised acid per litre, is used, each c.c. of this solution will represent 1 milligram of CO_2. This is more convenient in practice, since it saves calculation.

(e). *Turmeric-paper* (226), which has not lost its full yellow colour.

733. *The Process of Estimation.*—By means of the bellows (b) a volume of the air which is to be tested, equal to at least six times the capacity of the bottle, is blown down to the bottom of the bottle (a). The atmospheric temperature and the barometric pressure are then noted down. One hundred c.c. of the lime-water (c) are at once introduced into the bottle, and the rubber cork is inserted.

The bottle is laid on its side and rolled along on a level surface, so as to wet the interior with the lime-water; this is repeated several times during half an hour.

Forty c.c. of the liquid are withdrawn from the bottle, by means of a dry pipette with rubber tube attached to its top: and the bottle is immediately closed. Or the lime-water is rapidly poured off into a 200 c.c. stoppered measuring-vessel; the bottle is quickly rinsed out several times into the measuring-vessel with small quantities of freshly-boiled cold distilled water; and the volume of the liquid is finally made up to 200 c.c. with air-free water, and is well mixed by shaking it.

Either the 40 c.c. taken direct from the bottle (**a**), or an aliquot portion of the above diluted liquid, is then removed into a small flask, and is titrated by the standard oxalic acid (**d**). A small drop of the liquid is placed occasionally upon turmeric-paper, to ascertain when its alkaline reaction just disappears. The brown tint on the paper is last seen at the edge of the wet spot, just before it disappears completely.

At least one repetition of the titration should be made, so as to obtain accurately the volume of acid required. The volume of acid which would be required by the 100 c.c. of lime-water is then calculated.

A measured volume of the original lime-water (**c**) is then titrated with the standard acid ; and the volume of acid which would be required to neutralise 100 c.c. of this lime-water is calculated.

The difference between the volumes of acid which would be required for 100 c.c. of lime-water before and after its exposure to the sample of air, is a volume which contains an amount of oxalic acid chemically equivalent in neutralising power to the CO_2 which was present in the air of the bottle.

Throughout the whole of the manipulation in the above process, it is evidently necessary to guard as far as is possible against the further absorption of CO_2 from the open air or from the breath. This is secured by making the exposure of the lime-water to the open air as brief as possible. All distilled water used for dilution should also have been recently boiled and rapidly cooled, so as to be free from carbonic acid.

Baryta-water may be substituted for lime-water, but it presents no advantage : its saturated solution is stronger than that of lime-water, and must be somewhat diluted for use.

Deci-normal hydrochloric acid may conveniently replace the standard oxalic acid : it maintains its strength more satisfactorily than oxalic acid solution does, and in a diluted state it is free from action on the precipitated carbonate.

Example.—The results of an actual estimation were as follows.
Capacity of the bottle = 9200 c.c. ; temperature of the sample of air = 19° C. ; atmospheric pressure = 760 mm.

100 c.c. of the lime-water required 48·8 c.c. of standard oxalic acid solution, 1 c.c. of which corresponds to 0·002 of CO_2.

40 c.c. of the lime-water, after being shaken with the air-sample, required 17·9 c.c. of the standard acid; therefore

100 c.c. of this lime-water would require 44·75 c.c. of the standard acid.

Therefore the amount of CO_2 in the sample of air is equivalent to $48·8 - 44·75 = 4·05$ c.c. of standard acid.

But 1 c.c. of the acid is equivalent to 0·002 gram of CO_2; therefore the weight of CO_2 in the air-sample $= 4·05 \times 0·002 = 0·0081$ gram.

And the volume of the $CO_2 = \frac{0·0081}{0·0000896 \times 22} = 4·11$ c.c. at 0° C. and at 760 mm. pressure.

Hence the volume of CO_2 at $19° = 4·11 \times \frac{292}{273} = 4·395$ c.c.

And the percentage of $CO_2 = \frac{4·395 \times 100}{9200} = 0·048$.

734. The Following Series of Results, obtained by students in the chemical laboratory of the University College, Nottingham, will serve to indicate the varying degrees of efficiency attained in the ventilation of different buildings. They also indicate the effect on pure country air of polluted colliery air brought in by the wind.

The results are stated as percentages by volume of CO_2 in the air taken from the localities indicated.

The top of the Castle-rock; fresh air, . . .	0·038
University College, the grounds, ...	0·043
,, ,, the chemical laboratory, . .	0·069
Masonic Hall, lower room, 12 P.M., ...	0·179
,, ,, upper room, during dancing, . .	0·312
Circus building, promenade, 10 P.M., . . .	0·326
Private sitting-room, 1620 cubic feet capacity, open fireplace, closed for 3 hours with two persons and three gas-jets, ...	0·284
Committee-room, closed for 2¼ hours with fifteen persons and twenty-seven gas-jets, . . .	0·418
Wesleyan Chapel, near floor, after afternoon service, windows and doors closed, ...	0·218
Pasture fields, Derbyshire, wind from hills, bright morning, ...	0·030
Pasture fields, Derbyshire, wind from village and colliery, morning misty, ...	0·045

The above results serve as a measure of the adequacy of the ventilating arrangements, which varies inversely as the proportion of

carbon dioxide found in the air. The best ventilated building was the College laboratory, in which the sample was collected during evening work, while about thirty students were engaged in practical work with a corresponding number of Bunsen-burners and illuminating gas-jets.

The air from the colliery district was rendered impure by large burning heaps of waste, as well as by the air from the ventilating shafts of the "pits."

VAPOUR DENSITY DETERMINATIONS.

735. Introductory Remarks.—By the term "vapour density" is usually meant the specific gravity of a vapour referred to that of hydrogen as unity.

For chemical purposes, hydrogen is invariably the standard selected, and for the following reason. According to the theory now generally accepted, equal volumes of all gases and vapours, when compared under similar conditions, contain an equal number of molecules. Hence the specific gravity of a gas or vapour, if referred to hydrogen as unity, simply requires to be multiplied by 2, in order to yield the molecular weight of the gas or vapour. This method of determining molecular weights is therefore supplementary to those methods which have been already described (**674–676**).

Of the many methods which have been proposed for determining vapour densities, two only are described here.

The most recent one, that of Victor Meyer (**736**), has the advantage of being very simple as regards the apparatus used, the manipulation, and the calculation of the result; it further requires the use of a small amount of substance only.

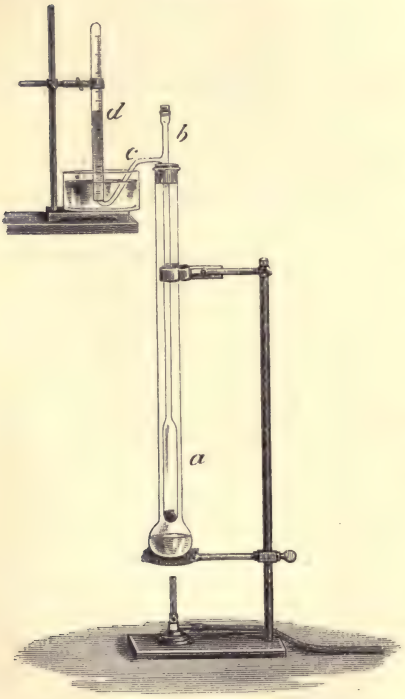
The second, that of Dumas (**739**), is more complicated in every respect, and requires a larger amount of substance.

The Meyer Vapour Density Method.

736. This method depends upon the determination of the volume of vapour which is yielded by a known weight of the volatile substance, by measuring the volume of air which

the vapour displaces. The volume of air thus displaced is measured at atmospheric temperature and pressure, and is saturated with aqueous vapour. Its volume in c.c., when dry and under normal conditions, is calculated (685, 2); and the weight of an equal volume of hydrogen is then obtained by multiplying this number by 0·0000896. When the weight of the substance taken is divided by this weight of hydrogen, the density of the vapour of the substance is obtained.

Fig. 103.



737. The Apparatus which is Employed for the determination is shown in fig. 103.

The inner vapour-tube (*b*) is shaped like a large thermometer. It is furnished near the top with a bent, thick-walled capillary delivery-tube (*c*). Its top is somewhat enlarged, and can be closed with a tightly fitting cork. The tube has a capacity of about 200 c.c.

A broad tube (*a*), which is enlarged into a bulb at the bottom, serves as a heating-jacket for the vapour-tube. A liquid is placed in the bulb of this jacket, which has a much higher boiling-point than that of the liquid whose vapour-density is to be determined.

Water is frequently used in the outer jacket, but bodies of higher boiling-point than water are often required. Amylic alcohol, aniline, and sulphur are amongst those most frequently employed. A suitable form of air-jacket may also be used. If the vapour-tube is made of porcelain, it may be immersed in melted lead or other metals, or in the vapour of boiling zinc.

A measuring-tube (*d*), of about 100 c.c. capacity and graduated into fifths of a c.c., is filled with water and is inverted in a vessel of water. This stands at a convenient height for collecting the air escaping through (*c*). A laboratory stool, placed upon the working bench, is generally of suitable height for supporting the vessel of water.

738. The Estimation is carried out as follows.—For practice in the method, the vapour-density of pure ether may be determined.

The ether is purified by washing it with salt water ; it is then dried by being shaken with powdered calcium chloride. It is freed from the last traces of water by dropping into it some clean slices of sodium, and allowing the liquid to stand for several hours in a loosely corked flask, until no more bubbles of hydrogen escape from the surface of the sodium. The ether is then distilled off through a dry condenser into a clean dry bottle, rejecting the first portion of the distillate. Only that portion of the distillate must be collected which boils at 34°·5 C.

The apparatus described above (**737**) is fitted up as is shown in fig. 103. A pad of dry asbestos is pushed down to the bottom of the vapour-tube, which is then closed by the cork ; the delivery-tube dipping under the water in the trough. The bulb of the jacket-tube is half-filled with water, which is kept boiling by the Bunsen-burner sufficiently vigorously to cause steam to escape from the loosely-corked top of the jacket.

As soon as no more air-bubbles escape from the delivery-tube (*c*) the cork is loosened in the top of the vapour-tube, since the air within it has reached steam-heat and the tube is therefore ready for the determination. The measuring-tube (*d*) is now clamped in position over the end of the delivery-tube (*c*).

Meanwhile a little glass tube about an inch in length is made out of quill tubing, one end being closed, and the other being drawn out to a capillary. The tube is weighed, and a suitable quantity of the pure ether is introduced into it, by heating the tube, and allowing it to cool with its capillary point immersed in the pure liquid. The tube is then re-weighed, with the capillary end open. Its gain in weight gives the weight of the ether taken for the experiment.

The little glass tube for containing the weighed liquid in the above process may be conveniently furnished with an accurately-fitting small stopper. This may be made by grinding a piece of glass rod into the mouth of the tube by wetted fine emery powder. The necessity of making a fresh tube for each determination is thus obviated.

The open tube containing the ether is then *at once* dropped into the vapour-tube, which is immediately closed by the cork. The ether will begin to boil, and its vapour will displace air from the vapour-tube, which will escape in a stream of bubbles into the measuring-tube. As soon as no more bubbles escape, the cork of the vapour-tube is removed.

The measuring-tube (d) is then removed to a tall cylinder of water, which should be at the temperature of the air. The tube is immersed in the water; and as soon as its contents have gained the temperature of the water, the tube is raised until the water inside and outside are at the same level. The volume of the air is then carefully read off; and the temperature of the water, and the barometric pressure, are noted at the same time.

Calculation of Results.—All the data, necessary for the calculation of the vapour-density of the ether, have now been obtained. According to paragraph 685, 2,

$$\text{The vapour density} = \frac{S \times 760 \times (1 + 0{\cdot}003665t)}{v \times (p - w) \times 0{\cdot}0000896}.$$

In which formula:—

S = weight of substance taken.

t = temperature of the water in the cylinder.

v = observed volume of air in c.c.
p = barometric pressure, reduced to 0°.
w = tension of water-vapour at t°.
0·0000896 = weight of 1 c.c. of hydrogen.

Example.—In a determination of the vapour density of ether, the following numbers were noted down :—

Weight of ether taken = 0·073 gram.
Temperature of water = 21·5 C.
Volume of air displaced = 25·3 c.c.
Barometric pressure at 0° = 718·6 mm.
Tension of aqueous vapour = 19·07 mm.

$$\text{The vapour density} = \frac{0{\cdot}073 \times 760 \times (1 + 0{\cdot}003665 \times 21{\cdot}5)}{25{\cdot}3 \times (718{\cdot}6 - 19{\cdot}07) \times 0{\cdot}0000896} = 36{\cdot}74.$$

The Dumas Vapour Density Method.

739. This method depends upon the determination of the weight of a definite volume of the vapour, measured at a known temperature and pressure. The volume of the vapour, under normal conditions of temperature and pressure, is then calculated (**685**, 1) : the weight of an equal volume of hydrogen is calculated ; and the vapour density is obtained by dividing the weight of the vapour by that of the hydrogen.

740. The Apparatus Required for the Process is shown in fig. 104. A large thin glass bulb, with its neck drawn out, is used for containing the vapour : it has a capacity of about 200 c.c. This may be purchased, or it may be made by drawing out the neck of a suitable round flask. The bulb can be supported in a double clamp, and immersed in a suitable liquid contained in a large vessel, preferably of metal : a large copper water-bath serves very well. The bath is placed on a tripod-stand, and is heated by a gas-burner. The temperature of the liquid in the bath is taken by means of a thermometer, the bulb of which is placed near the middle of the vapour-bulb.

741. The Process of Estimation is conducted as follows. For practice in the process, the vapour density of pure benzene may be determined.

The empty apparatus having been arranged as is shown in the figure, the bulb is removed together with its clamp. The bath is then nearly filled with liquid,—in this case water, which is heated to boiling.

Meanwhile the clean, dry bulb is weighed after remaining in the balance-case for some time. About 20 c.c. of the

FIG. 104.

benzene are then introduced into the bulb, by heating it and allowing it to cool with its open end immersed in the liquid.

The bulb is now fixed in its clamps and is immersed in the gently-boiling water in the bath, with the end of the tube projecting about half an inch above the surface of the water. It is clamped in this position. The thermometer is

also at once fixed, with its bulb level with the middle of the vapour-bulb and close to it.

The benzene will boil vigorously: and the vapour which it evolves will issue violently from the neck, expelling the air from the bulb. After the vapour has issued for some time and escapes more quietly, it may be kindled at the end of the tube. The dropping of the flame serves to indicate the moment at which the issue of vapour ceases. The end of the tube is then at once sealed by bringing a blowpipe-flame to bear upon it. At this moment the temperature shown by the thermometer immersed in the bath, and the barometric pressure, are read.

The bulb is then removed from the bath, and is at once thoroughly dried. It is allowed to cool, and is placed in the balance-case for some time. Its weight is then taken, the temperature of the air in the balance-case being noted.

A file-scratch is now made near the sealed end of the tube of the bulb; and the end is broken off under some water, which has been freed from air by having been recently boiled for some time and then rapidly cooled. The bulb will fill with water. The volume of any air-bubble which remains in the bulb may be found by transferring it to the neck, and measuring its dimensions. The water is then allowed to flow out into a graduated measuring-cylinder. The volume of the water, together with that of any air-bubble which was in the bulb, will give the capacity of the bulb, when the volume has been reduced to absolute c.c. if necessary (**203**).

742. Calculation of Results.—All the data for calculating the vapour density have now been obtained (**685**, 2). They are the following:—

g = weight of bulb.
G = apparent weight of bulb filled with vapour.
t = temperature of air, second weighing.
T = temperature of bath, at sealing.
p = barometric pressure, reduced to 0°.
c = capacity of bulb in c.c.

The Weight of the Vapour.—Neglecting certain corrections of minor importance, the weight of the vapour which filled the bulb is obtained by subtracting the weight of the bulb from the apparent weight of the bulb and vapour, and adding the weight of the volume of air which was displaced by the bulb at the temperature and pressure of the last weighing. Accordingly :—

$$\text{Weight of vapour} = G - g + \frac{c \times p \times 0{\cdot}001293}{760(1 + 0{\cdot}003665t)}.$$

The Weight of the Hydrogen, which would fill the bulb at the temperature of the bath, and at the barometric pressure, will be found by the following expression :—

$$\text{Weight of hydrogen} = \frac{c \times p \times 0{\cdot}0000896}{760(1 + 0{\cdot}003665T)}.$$

The Vapour Density will be found by dividing the weight of the vapour which fills the bulb, by the weight of an equal volume of hydrogen under the same conditions. Accordingly, it is obtained from the results of the above calculations by the expression :—

$$\text{The vapour density} = \frac{\text{weight of vapour}}{\text{weight of hydrogen}}.$$

Example.—In a determination of vapour density,

Weight of the bulb = 23·683 grams.
Apparent weight of the bulb + vapour = 23·957 grams.
Temperature of air = 16° C.
Temperature of bath = 112° C.
Barometric pressure = 755 mm.
Capacity of bulb = 180 c.c.

Therefore the weight of vapour at 112° filling the bulb (x)

$$= 23{\cdot}957 - 23{\cdot}683 + \frac{180 \times 755 \times 0{\cdot}001293}{760(1 + 0{\cdot}003665 \times 16)}.$$

And the weight of an equal volume of hydrogen (y)

$$= \frac{180 \times 755 \times 0{\cdot}0000896}{760(1 + 0{\cdot}003665 \times 112)}.$$

Therefore the vapour density $= \frac{x}{y} = 43{\cdot}35.$

APPENDIX.

TABLES FOR REFERENCE, &c.

750. Introductory Remarks. The Appendix contains information of general use to the Analyst.

Section I. includes the statement of Results of Typical Analyses (751–772) made by processes described in the text. These will be found useful for the purpose of comparison with the results obtained by the student.

A Table of Atomic Weights of the Elements follows (773), together with a list of Factors (774), which will be found useful in calculating the results obtained by gravimetric analysis.

Kopp's Table for the Expansion of Water by heat (775) is added for the calculation of results in calibrating measuring-vessels (203, 207): and Alcohol Tables (776, 777) for calculating the percentage of alcohol present in a liquid, from its specific gravity (604).

A Table of Factors for converting the Volume of a gas at any temperature and pressure to its Normal Volume at 0° C. and 760 mm. pressure (778), will be found most useful in gas analysis and in vapour density determinations: as will also Regnault's Table giving the Tension of Aqueous Vapour at all atmospheric temperatures (779).

This Section concludes with formulæ for converting the

ordinary Thermometric Scales (780): Tables of French and English Weights and Measures (781–783): and some useful Memoranda (784).

Section II. contains information concerning the Apparatus and Chemicals required for use in Quantitative Analysis. The information is supplementary to that given in Section VII. of *Clowes' Practical Chemistry.*

A short account of a General Apparatus for the Preparation of certain Gases (786), and of a useful form of Still for the Preparation of Distilled Water (787, 788), is followed by Lists of the Apparatus, Reagents, and the Substances required for Experiments and for Analysis (789–792), which are mentioned in the book.

The Appendix concludes with a list of the Processes of Separation which are described in the text (793).

SECTION I.

RESULTS OF TYPICAL ANALYSES.

Note.—The numbers given are percentages, unless a statement is made to the contrary.

751. Dolomite, or Magnesian Limestone.

Carbon dioxide,	45·64
Silica,	1·38
Iron and Aluminium oxides,	1·38
Calcium oxide,	30·83
Magnesium oxide,	20·99

752. Spathic Iron-Ore.

Ferrous oxide,	49·77
Ferric oxide,	0·81
Manganese oxide,	1·93
Calcium oxide,	3·96
Magnesium oxide,	2·83
Carbon dioxide,	37·20
Phosphorus pentoxide,	Trace
Sulphur,	0·04
Water,	0·30
Insoluble residue,	3·12

753. Salt Cake.

Water,	0·05
Insoluble matter,	0·19
Iron and aluminium oxides,	0·14
Calcium oxide,	0·20
Magnesium oxide,	0·13
Sulphur trioxide,	57·17
Chlorine,	0·02
Sodium oxide,	41·86

754. Felspar.

Silica,	65·14
Iron and Aluminium oxides,	18·68
Calcium oxide,	0·47
Magnesium oxide,	0·36
Potassium oxide,	11·82
Sodium oxide,	3·37

755. Glass.

	I.	II.	III.
Silica,	71·71	70·71	51·40
Potassium oxide,	12·70	...	9·40
Sodium oxide,	2·50	13·25	...
Calcium oxide,	10·30	13·38	...
Lead oxide,	...	...	37·40
Iron and Aluminium oxides,	9·60	1·92	2·00

I. Bohemian glass. II. Window glass. III. Flint glass.

756. Zinc Blende.

Insoluble residue,	14·43
Copper,	1·81
Iron,	12·61
Sulphur,	28·40
Zinc,	43·06

Corresponding to ZnS, 64·2; FeS, 19·8.

757. Galena.

Sulphur,	13·90
Lead,	83·58
Iron,	0·83
Manganese,	1·26
Silver,	0·14

758. Copper Pyrites.

Sulphur,	35·16
Copper,	30·00
Iron,	32·20
Insoluble residue,	2·64

759. Brass.

Copper,	70·30
Zinc,	29·30
Tin,	0·17
Lead,	0·28

760. Bronze Coin.

Copper,	94·85
Tin,	3·90
Zinc,	1·14

761. Type Metal.

Lead,	61·30
Antimony,	18·80
Tin,	20·20

762. German Silver.

Copper,	62·40
Zinc,	22·15
Nickel,	15·05
Iron,	Trace.

763. Red Hæmatite Ores.

	I.	II.
Ferric oxide,	86·50	93·75
Manganous oxide,	0·21	Trace.
Aluminium oxide,	...	0·73
Calcium oxide,	2·77	0·61
Magnesium oxide,	1·46	0·23
Sulphur,	...	0·03
Sulphur trioxide,	0·11	...
Carbon dioxide,	2·96	...
Phosphorus pentoxide,	Trace.	0·32
Water, and organic matter,	...	1·09
Silica, and insoluble matter,	6·55	3·27

I. Ore from Ulverstone, Cumberland. II. Ore from Lake Superior.

764. Caking Coal.

Moisture,	4·36
Volatile matter,	35·92
Coke,	57·94
Ash,	1·78
Sulphur,	2·11
Calorific power,	7484

765. Superphosphate of Lime.

Moisture,	15·00
Organic matter,	12·00
Soluble phosphate,	18·00
[Equal to $Ca_3(PO_4)_2$],	[28·28]
Insoluble phosphate,	6·00
Calcium sulphate,	41·95
Alkalis, &c.,	0·55
Sand,	6·50

766. Cambridge Coprolites.

Moisture, Combined water, Organic matter,	4·04
Silicious matter,	8·19
Calcium phosphate,	58·09
Calcium carbonate,	21·12
Iron oxide,	2·18
Alumium oxide	2·05
Magnesium oxide, alkalis, &c.,	4·33

767. Bone Flour.

Moisture,	8·45
*Organic matter,	17·29
Calcium phosphate,	63·99
†Calcium carbonate, &c.,	8·97
Sand,	1·30
*Containing nitrogen,	1·35
(Equal to ammonia),	1·6
†Containing calcium oxide,	4·57

768. Peruvian Guano.

Moisture,	9·71
*Organic matter,	40·19
Calcium phosphate, $Ca_3(PO_4)_2$,	19·00
†Alkalis, &c.,	13·05
Sand,	18·05
*Containing nitrogen,	8·45
Equal to ammonia,	10·26
†Containing P_2O_5,	0·40
Equal to $Ca_3(PO_4)_2$,	0·87
Total P_2O_5,	9·10
Equal to $Ca_3(PO_4)_2$,	19·87

769. Basic Slag.

Moisture,	0·13
Calcium oxide,	32·42
*Phosphorus pentoxide,	18·44
Ferrous oxide, &c.,	39·46
Silica,	9·55
*Equal to $Ca_3(PO_4)_2$,	40·26

770. Water from Shallow Well.

	Parts per 100,000.
Total solids,	69·5
Free ammonia,	0·001
Albuminoid ammonia,	0·008
Oxygen consumed,	0·005
Chlorine,	4·8
Nitrite,	Nil.
Nitrogen as nitrate,	2·83
Temporary hardness,	15·4
Permanent ,,	23·4
Total ,,	38·8

771. Pale Resin Soap.

Fatty anhydride,	48·44
Sodium oxide (soda) in combination,	6·85
Resin,	23·97
Sodium silicate,	0·29
Silica,	0·55
Sodium carbonate,	1·53
Sodium hydrate (caustic soda),	Trace.
Insoluble matter,	Trace.
Water,	18·37

772. Coal Gas.

Carbon dioxide,	0·0
Oxygen,	0·2
Olefines and Benzenes,	5·3
Carbon monoxide,	6·6
Methane,	34·2
Hydrogen,	48·2
Nitrogen (by difference),	5·5

773. ATOMIC WEIGHTS OF THE ELEMENTS.

The numbers are those given in *Ostwald's Outlines of General Chemistry*, except when otherwise stated.

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
Aluminium	Al	27·08	Nickel	Ni	59·00
Antimony	Sb	120·30	Niobium	Nb	94·20
Arsenic	As	75·00	Nitrogen	N	14·04
Barium	Ba	137·00	Osmium	Os	190·77**
Beryllium	Be	9·05*	**Oxygen**	**O**	**16**
Bismuth	Bi	208·92†	Palladium	Pd	106·61††
Boron	B	11·01	Phosphorus	P	31·03
Bromine	Br	79·96	Platinum	Pt	195·5 ‡‡
Cadmium	Cd	111·80‡	Potassium	K	39·14
Cæsium	Cs	132·90	Rhodium	Rh	103·00
Calcium	Ca	40·00	Rubidium	Rb	85·40
Carbon	C	12·00	Ruthenium	Ru	101·70
Cerium	Ce	140·20	Samarium	Sa	150·00
Chlorine	Cl	35·45	Scandium	Sc	44·10
Chromium	Cr	52·20	Selenion	Se	79·10
Cobalt	Co	59·00	Silicon	Si	28·04
Copper	Cu	63·30	Silver	Ag	107·938
Didymium	D	142·50	Sodium	Na	23·06
Erbium	E	166·00	Strontium	Sr	87·50
Fluorine	F	19·00	Sulphur	S	32·06
Gallium	G	69·90	Tantalum	Ta	183·00
Germanium	Ge	72·30	Tellurion	Te	125·00
Gold	Au	197·20	Terbium	Tr	159·48§§
Hydrogen	H	1·003	Thallium	Tl	204·10
Indium	In	113·70	Thorium	Th	232·40
Iodine	I	126·86	Tin	Sn	119·1 ‖‖
Iridium	Ir	193·20	Titanium	Ti	48·10
Iron	Fe	56·00	Tungsten	W	184·8
Lanthanum	La	138·22§	Uranium	U	239·40
Lead	Pb	206·91	Vanadium	V	51·20
Lithium	L	7·03	Ytterbium	Yb	173·20
Magnesium	Mg	24·33‖	Yttrium	Y	89·02‖
Manganese	Mn	55·05¶	Zinc	Zn	65·50
Mercury	Hg	200·40	Zirconium	Zr	90·70
Molybdenum	Mo	95·90			

* Krüss and Moraht.
† Classen.
‡ Partridge.
§ Cleve.
‖ Marignac, and Burton and Vorce (mean number).
¶ Marignac, and Dewar and Scott (mean number).
** Seubert.
†† Keiser.
‡‡ Dittmar and M'Arthur.
§§ Boisbaudran.
‖‖ Bongartz and Classen.

FACTORS FOR QUANTITATIVE ANALYSIS.

774. The following factors, or their logarithms, may be used to facilitate the calculation of results obtained by gravimetric analysis. The weight of the substance standing in the second column, when multiplied by the factor, furnishes the corresponding weight of the substance standing on the same line in the first column. Thus the weight of Ag in 0·64 gram of AgCl = 0·64 × 0·75277 = 0·48177.

Required.	Weighed as.	Factor.	Logarithm.
Ag	AgCl	0·75277	$\bar{1}$·87666
AgCl	Ag	1·32843	0·12334
AgBr	Ag	1·74080	0·24075
Al	Al_2O_3	0·53015	$\bar{1}$·72440
As	As_2S_3	0·60931	$\bar{1}$·78484
As	$Mg_2As_2O_7$	0·48284	$\bar{1}$·68380
As_2O_3	As_2S_3	0·80430	$\bar{1}$·90542
As_2O_3	$Mg_2As_2O_7$	0·63735	$\bar{1}$·80438
As_2O_5	As_2S_3	0·93429	$\bar{1}$·97048
As_2O_5	$Mg_2As_2O_7$	0·74036	$\bar{1}$·86944
AsO_4	As_2S_3	1·12925	0·05279
AsO_4	$Mg_2As_2O_7$	0·89485	$\bar{1}$·95175
Ba	$BaSO_4$	0·58783	$\bar{1}$·76925
BaO	$BaSO_4$	0·65648	$\bar{1}$·81722
Bi	Bi_2O_3	0·89696	$\bar{1}$·95277
B_2O_3	AgCl	0·48833	$\bar{1}$·68871
Br	AgBr	0·42555	$\bar{1}$·62895
Cd	CdS	0·77714	$\bar{1}$·89050
CdO	CdS	0·88836	$\bar{1}$·94859
Ca	CaO	0·71429	$\bar{1}$·85387
Ca	$CaCO_3$	0·40000	$\bar{1}$·60206
CaO	$CaCO_3$	0·56000	$\bar{1}$·74819

Required.	Weighed as.	Factor.	Logarithm.
C	CO_2	0·27273	$\bar{1}$·43573
CO_3	CO_2	1·36364	0·13470
Cl	AgCl	0·24724	$\bar{1}$·39311
ClO_3	AgCl	0·58200	$\bar{1}$·76492
CN	Ag	0·24125	$\bar{1}$·38247
CN	AgCN	0·19436	$\bar{1}$·28861
Cr	Cr_2O_3	0·68505	$\bar{1}$·83572
CrO_3	Cr_2O_3	1·31496	0·11891
CrO_4	Cr_2O_3	1·52493	0·18325
CoO	Co	1·27119	0·10421
Cu	CuO	0·79823	$\bar{1}$·90213
Cu	Cu_2S	0·79792	$\bar{1}$·90196
CuO	Cu_2S	1·00000	0·00000
F	CaF_2	0·48718	$\bar{1}$·68769
Fe	Fe_2O_3	0·70000	$\bar{1}$·84510
H	H_2O	0·11141	$\bar{1}$·04691
HCl	AgCl	0·25423	$\bar{1}$·40522
HCN	AgCN	0·20185	$\bar{1}$·30502
Hg	HgS	0·86209	$\bar{1}$·93555
H_2SO_4	$BaSO_4$	0·42088	$\bar{1}$·62405
I	AgI	0·54029	$\bar{1}$·73263
K	K_2SO_4	0·44900	$\bar{1}$·65225
K	K_2PtCl_6	0·16091	$\bar{1}$·20658
K_2O	K_2SO_4	0·54078	$\bar{1}$·73302
K_2O	K_2PtCl_6	0·19380	$\bar{1}$·28735
K_2O	KCl	0·63199	$\bar{1}$·80071
KCl	K_2PtCl_6	0·30665	$\bar{1}$·48664
Mg	$Mg_2P_2O_7$	0·21848	$\bar{1}$·33941
MgO	$Mg_2P_2O_7$	0·36216	$\bar{1}$·55890
Mn	Mn_3O_4	0·72071	$\bar{1}$·85776
MnO	Mn_3O_4	0·93019	$\bar{1}$·96857
MnO_4	Mn_3O_4	1·55858	0·19273
Na	Na_2SO_4	0·32438	$\bar{1}$·51105

Required.	Weighed as.	Factor.	Logarithm.
Na	NaCl	0·39412	$\bar{1}$·59563
Na_2O	Na_2SO_4	0·43691	$\bar{1}$·64039
Na_2O	NaCl	0·53085	$\bar{1}$·72497
Ni	NiO	0·78667	$\bar{1}$·89579
N	Pt	0·14363	$\bar{1}$·15725
N	$(NH_4)_2PtCl_6$	0·06320	$\bar{2}$·80072
NH_3	Pt	0·17441	$\bar{1}$·24158
NH_3	$(NH_4)_2PtCl_6$	0·07674	$\bar{2}$·88505
NH_4	Pt	0·18468	$\bar{1}$·26641
NH_4	$(NH_4)_2PtCl_6$	0·08126	$\bar{2}$·90988
Pb	PbO	0·92822	$\bar{1}$·96765
Pb	$PbSO_4$	0·68294	$\bar{1}$·83438
PbO	$PbSO_4$	0·73575	$\bar{1}$·86673
P	$Mg_2P_2O_7$	0·27864	$\bar{1}$·44505
P_2O_5	$Mg_2P_2O_7$	0·63784	$\bar{1}$·80471
PO_4	$Mg_2P_2O_7$	0·85336	$\bar{1}$·93113
Sb	Sb_2S_3	0·71441	$\bar{1}$·85395
Sb	Sb_2O_4	0·78990	$\bar{1}$·89757
Sb_2O_3	Sb_2S_3	0·85694	$\bar{1}$·93295
Sb_2O_3	Sb_2O_4	0·94748	$\bar{1}$·97657
Si	SiO_2	0·46703	$\bar{1}$·66934
Sn	SnO_2	0·78822	$\bar{1}$·89665
Sr	$SrSO_4$	0·47668	$\bar{1}$·67823
SrO	$SrSO_4$	0·56385	$\bar{1}$·75116
S	$BaSO_4$	0·13756	$\bar{1}$·13849
SO_2	$BaSO_4$	0·27487	$\bar{1}$·43912
SO_3	$BaSO_4$	0·34352	$\bar{1}$·53595
SO_4	$BaSO_4$	0·41216	$\bar{1}$·61507
S_2O_3	$BaSO_4$	0·24054	$\bar{1}$·38118
Zn	ZnO	0·80368	$\bar{1}$·90508
Zn	ZnS	0·67138	$\bar{1}$·82697
ZnO	ZnS	0·83539	$\bar{1}$·92189

775. Expansion of Water (*Kopp*).

Temperature, Centigrade.	Volume (Volume at 0°=1).	Density (Density at 0°=1).	Volume (Volume at 4°=1).	Density (Density at 4°=1).
0°	1·00000	1·000000	1·00012	0·999877
1	0·99995	1·000053	1·00007	0·999930
2	0·99991	1·000092	1·00003	0·999969
3	0·99989	1·000115	1·00001	0·999992
4	0·99988	1·000123	1·00000	1·000000
5	0·99988	1·000117	1·00001	0·999994
6	0·99990	1·000097	1·00003	0·999973
7	0·99994	1·000062	1·00006	0·999939
8	0·99999	1·000014	1·00011	0·999890
9	1·00005	0·999952	1·00017	0·999829
10	1·00012	0·999876	1·00025	0·999753
11	1·00021	0·999785	1·00034	0·999664
12	1·00031	0·999686	1·00044	0·999562
13	1·00043	0·999572	1·00055	0·999449
14	1·00056	0·999445	1·00068	0·999322
15	1·00070	0·999306	1·00082	0·999183
16	1·00085	0·999155	1·00097	0·999032
17	1·00101	0·998992	1·00113	0·998869
18	1·00118	0·998817	1·00131	0·998695
19	1·00137	0·998631	1·00149	0·998509
20	1·00157	0·998435	1·00169	0·998312
21	1·00178	0·998228	1·00190	0·998104
22	1·00200	0·998010	1·00212	0·997886
23	1·00223	0·997780	1·00235	0·997657
24	1·00247	0·997541	1·00259	0·997419
25	1·00271	0·997293	1·00284	0·997170
26	1·00295	0·997035	1·00310	0·996912
27	1·00319	0·996767	1·00337	0·996644
28	1·00347	0·996489	1·00365	0·996367
29	1·00376	0·996202	1·00393	0·996082
30	1·00406	0·996008	1·00423	0·995787

ALCOHOL TABLE I.

776. PERCENTAGE OF ABSOLUTE ALCOHOL, BY WEIGHT AND VOLUME, CORRESPONDING TO THE SPECIFIC GRAVITY TAKEN AT 60° F., OR 15°·5 C. WATER = 1.

I. Percentage of Alcohol by Volume.				II. Percentage of Alcohol by Weight.			
Per cent.	Specific Gravity.	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.
0	1·0000	50	0·9343	0	1·0000	50	0·9183
1	0·9985	51	0·9323	1	0·9981	51	0·9160
2	0·9970	52	0·9303	2	0·9963	52	0·9138
3	0·9956	53	0·9283	3	0·9944	53	0·9116
4	0·9942	54	0·9263	4	0·9928	54	0·9049
5	0·9928	55	0·9242	5	0·9912	55	0·9072
6	0·9915	56	0·9221	6	0·9896	56	0·9049
7	0·9902	57	0·9200	7	0·9880	57	0·9027
8	0·9890	58	0·9178	8	0·9866	58	0·9004
9	0·9878	59	0·9156	9	0·9852	59	0·8981
10	0·9866	60	0·9134	10	0·9839	60	0·8958
11	0·9854	61	0·9112	11	0·9826	61	0·8935
12	0·9843	62	0·9090	12	0·9813	62	0·8911
13	0·9832	63	0·9067	13	0·9800	63	0·8888
14	0·9821	64	0·9044	14	0·9788	64	0·8865
15	0·9811	65	0·9021	15	0·9775	65	0·8842
16	0·9800	66	0·8997	16	0·9763	66	0·8818
17	0·9790	67	0·8973	17	0·9751	67	0·8795
18	0·9780	68	0·8949	18	0·9739	68	0·8772
19	0·9770	69	0·8925	19	0·9727	69	0·8748
20	0·9760	70	0·8900	20	0·9714	70	0·8724
21	0·9750	71	0·8875	21	0·9702	71	0·8700
22	0·9740	72	0·8850	22	0·9690	72	0·8676
23	0·9729	73	0·8825	23	0·9677	73	0·8652
24	0·9719	74	0·8799	24	0·9664	74	0·8629
25	0·9709	75	0·8773	25	0·9651	75	0·8605
26	0·9698	76	0·8747	26	0·9637	76	0·8581
27	0·9688	77	0·8720	27	0·9622	77	0·8557
28	0·9677	78	0·8693	28	0·9607	78	0·8533
29	0·9666	79	0·8666	29	0·9592	79	0·8509
30	0·9655	80	0·8639	30	0·9577	80	0·8484
31	0·9643	81	0·8611	31	0·9560	81	0·8459
32	0·9631	82	0·8583	32	0·9544	82	0·8435
33	0·9618	83	0·8555	33	0·9526	83	0·8409
34	0·9605	84	0·8526	34	0·9508	84	0·8385
35	0·9592	85	0·8496	35	0·9490	85	0·8359
36	0·9579	86	0·8466	36	0·9472	86	0·8333
37	0·9565	87	0·8436	37	0·9453	87	0·8307
38	0·9550	88	0·8405	38	0·9433	88	0·8282
39	0·9535	89	0·8373	39	0·9413	89	0·8256
40	0·9519	90	0·8339	40	0·9394	90	0·8229
41	0·9503	91	0·8306	41	0·9374	91	0·8203
42	0·9487	92	0·8272	42	0·9353	92	0·8176
43	0·9470	93	0·8237	43	0·9332	93	0·8149
44	0·9452	94	0·8201	44	0·9311	94	0·8122
45	0·9435	95	0·8164	45	0·9291	95	0·8094
46	0·9417	96	0·8125	46	0·9269	96	0·8065
47	0·9399	97	0·8084	47	0·9249	97	0·8036
48	0·9381	98	0·8047	48	0·9227	98	0·8006
49	0·9362	99	0·7995	49	0·9204	99	0·7976
50	0·9343	100	0·7946	50	0·9183	100	0·7946

ALCOHOL TABLE II.

777. PERCENTAGE BY WEIGHT OF ABSOLUTE ALCOHOL AND OF PROOF-SPIRIT IN DILUTE ALCOHOL OF KNOWN SPECIFIC GRAVITY. WATER = 1000.

Specific Gravity at 60° F. or 15°·5 C.	Absolute Alcohol per cent. by Weight.	Per cent. of Proof-spirit.	Specific Gravity at 60° F. or 15°·5 C.	Absolute Alcohol per cent. by Weight.	Per cent. of Proof-spirit.	Specific Gravity at 60° F. or 15°·5 C.	Absolute Alcohol per cent. by Weight.	Per cent. of Proof-spirit.
995·0	2·74	6·02	992·8	4·02	8·81	990·6	5·39	11·79
994·9	2·79	6·13	992·7	4·08	8·94	990·5	5·45	11·92
994·8	2·85	6·26	992·6	4·14	9·07	990·4	5·51	12·05
994·7	2·91	6·39	992·5	4·20	9·20	990·3	5·58	12·20
994·6	2·97	6·52	992·4	4·27	9·36	990·2	5·64	12·33
994·5	3·02	6·63	992·3	4·33	9·49	990·1	5·70	12·46
994·4	3·08	6·76	992·2	4·39	9·62	990·0	5·77	12·61
994·3	3·14	6·89	992·1	4·45	9·75			
994·2	3·20	7·02	992·0	4·51	9·88	989·9	5·83	12·74
994·1	3·26	7·16				989·8	5·88	12·87
994·0	3·32	7·29	991·9	4·57	10·01	989·7	5·96	13·02
			991·8	4·64	10·16	989·6	6·02	13·15
993·9	3·37	7·40	991·7	4·70	10·29	989·5	6·09	13·30
993·8	3·43	7·53	991·6	4·76	10·42	989·4	6·15	13·43
993·7	3·49	7·66	991·5	4·82	10·55	989·3	6·22	13·59
993·6	3·55	7·79	991·4	4·88	10·68	989·2	6·29	13·74
993·5	3·61	7·92	991·3	4·94	10·81	989·1	6·35	13·87
993·4	3·67	8·05	991·2	5·01	10·96	989·0	6·42	14·02
993·3	3·73	8·18	991·1	5·07	11·09			
993·2	3·78	8·29	991·0	5·13	11·22	988·9	6·49	14·17
993·1	3·84	8·42				988·8	6·55	14·30
993·0	3·90	8·55	990·9	5·20	11·38	988·7	6·62	14·45
			990·8	5·26	11·51	988·6	6·69	14·60
992·9	3·96	8·68	990·7	5·32	11·64	988·5	6·75	14·73

778. FACTORS FOR CONVERTING THE

The following Table will be found useful for converting the volume volume under normal conditions. The normal volume is

	7°	8°	9°	10°	11°	12°	13°	14°
730	·9365	·9332	·9299	·9266	·9233	·9201	·9169	·9137
731	·9378	·9345	·9311	·9278	·9246	·9214	·9182	·9150
732	·9391	·9357	·9324	·9291	·9258	·9226	·9194	·9162
733	·9404	·9370	·9337	·9304	·9271	·9239	·9207	·9175
734	·9416	·9383	·9350	·9317	·9284	·9252	·9220	·9187
735	·9429	·9396	·9362	·9329	·9297	·9264	·9232	·9200
736	·9442	·9408	·9375	·9342	·9309	·9276	·9244	·9212
737	·9455	·9421	·9388	·9354	·9321	·9288	·9255	·9225
738	·9468	·9434	·9401	·9368	·9335	·9302	·9269	·9237
739	·9481	·9447	·9413	·9381	·9348	·9315	·9282	·9250
740	·9493	·9459	·9426	·9393	·9360	·9327	·9294	·9262
741	·9506	·9472	·9439	·9406	·9373	·9340	·9307	·9275
742	·9519	·9485	·9452	·9419	·9386	·9352	·9320	·9287
743	·9532	·9498	·9464	·9431	·9398	·9365	·9332	·9300
744	·9545	·9511	·9477	·9444	·9411	·9378	·9345	·9312
745	·9558	·9523	·9490	·9457	·9424	·9390	·9357	·9325
746	·9570	·9536	·9502	·9469	·9436	·9403	·9370	·9337
747	·9583	·9549	·9515	·9482	·9449	·9416	·9383	·9350
748	·9596	·9562	·9528	·9495	·9462	·9428	·9395	·9362
749	·9609	·9575	·9541	·9507	·9474	·9441	·9408	·9375
750	·9622	·9587	·9554	·9520	·9486	·9453	·9421	·9387
751	·9635	·9600	·9566	·9533	·9499	·9466	·9434	·9400
752	·9647	·9613	·9579	·9545	·9512	·9478	·9446	·9412
753	·9660	·9626	·9592	·9558	·9524	·9491	·9459	·9425
754	·9673	·9638	·9604	·9571	·9536	·9503	·9471	·9437

VOLUME OF A GAS TO 0° C. AND 760 MM.

of a gas, measured at ordinary temperature and pressure, into its obtained by multiplying the observed volume by the factor.

—	15°	16°	17°	18°	19°	20°	21°	22°
730	·9105	·9074	·9042	·9011	·8980	·8950	·8919	·8887
731	·9118	·9086	·9055	·9023	·8993	·8962	·8932	·8899
732	·9130	·9099	·9067	·9035	·9005	·8974	·8944	·8911
733	·9143	·9111	·9079	·9048	·9017	·8986	·8956	·8923
734	·9155	·9123	·9092	·9060	·9030	·8999	·8968	·8935
735	·9168	·9136	·9104	·9072	·9042	·9011	·8980	·8948
736	·9180	·9148	·9116	·9085	·9054	·9023	·8993	·8960
737	·9193	·9161	·9129	·9098	·9067	·9035	·9005	·8972
738	·9205	·9172	·9141	·9110	·9079	·9047	·9017	·8984
739	·9218	·9186	·9153	·9122	·9091	·9059	·9029	·8996
740	·9230	·9198	·9166	·9135	·9103	·9071	·9041	·9009
741	·9243	·9211	·9178	·9147	·9116	·9084	·9054	·9021
742	·9255	·9223	·9191	·9159	·9128	·9096	·9066	·9033
743	·9268	·9236	·9203	·9172	·9140	·9108	·9078	·9045
744	·9280	·9248	·9215	·9184	·9153	·9120	·9090	·9057
745	·9293	·9261	·9228	·9197	·9165	·9133	·9102	·9070
746	·9305	·9273	·9240	·9209	·9177	·9145	·9115	·9082
747	·9318	·9285	·9252	·9221	·9190	·9157	·9127	·9094
748	·9330	·9297	·9265	·9234	·9202	·9169	·9139	·9106
749	·9343	·9310	·9277	·9246	·9214	·9182	·9151	·9118
750	·9354	·9322	·9290	·9258	·9226	·9194	·9164	·9130
751	·9367	·9335	·9302	·9270	·9239	·9206	·9176	·9143
752	·9379	·9347	·9314	·9283	·9251	·9218	·9188	·9155
753	·9392	·9360	·9327	·9295	·9263	·9231	·9200	·9167
754	·9404	·9372	·9339	·9307	·9276	·9243	·9212	·9179

FACTORS FOR CONVERTING THE VOLUME

—	7°	8°	9°	10°	11°	12°	13°	14°
755	·9686	·9651	·9617	·9583	·9548	·9516	·9484	·9450
756	·9699	·9664	·9630	·9596	·9561	·9528	·9496	·9462
757	·9712	·9677	·9643	·9609	·9574	·9541	·9509	·9475
758	·9724	·9690	·9655	·9621	·9587	·9554	·9522	·9487
759	·9737	·9702	·9668	·9633	·9600	·9566	·9535	·9500
760	·9750	·9715	·9681	·9646	·9613	·9579	·9547	·9512
761	·9763	·9728	·9693	·9659	·9625	·9591	·9560	·9525
762	·9776	·9741	·9706	·9672	·9638	·9604	·9572	·9537
763	·9788	·9754	·9719	·9684	·9650	·9617	·9585	·9550
764	·9801	·9766	·9732	·9697	·9663	·9630	·9598	·9562
765	·9814	·9779	·9744	·9710	·9676	·9642	·9610	·9575
766	·9827	·9792	·9757	·9722	·9688	·9655	·9623	·9587
767	·9840	·9805	·9770	·9735	·9701	·9668	·9635	·9600
768	·9853	·9817	·9783	·9748	·9714	·9680	·9648	·9612
769	·9865	·9830	·9795	·9760	·9726	·9693	·9660	·9625
770	·9878	·9843	·9808	·9773	·9739	·9705	·9673	·9637
771	·9891	·9856	·9821	·9786	·9752	·9718	·9685	·9650
772	·9904	·9868	·9834	·9798	·9764	·9731	·9698	·9662
773	·9917	·9881	·9846	·9811	·9777	·9743	·9710	·9675
774	·9930	·9894	·9859	·9824	·9790	·9751	·9723	·9687
775	·9942	·9907	·9872	·9836	·9802	·9768	·9735	·9700
776	·9955	·9919	·9884	·9849	·9815	·9781	·9748	·9712
777	·9968	·9932	·9897	·9862	·9828	·9794	·9760	·9725
778	·9981	·9945	·9910	·9874	·9840	·9806	·9773	·9737
779	·9994	·9958	·9923	·9887	·9853	·9819	·9785	·9750
780	1·0007	·9971	·9935	·9899	·9866	·9831	·9798	·9762

OF A GAS TO 0° C. AND 760 MM.—(*Continued*).

—	15°	16°	17°	18°	19°	20°	21°	22°
755	·9417	·9385	·9351	·9320	·9288	·9255	·9225	·9191
756	·9429	·9397	·9364	·9332	·9300	·9267	·9237	·9204
757	·9442	·9410	·9376	·9344	·9313	·9280	·9249	·9216
758	·9454	·9422	·9389	·9357	·9325	·9292	·9261	·9228
759	·9467	·9434	·9401	·9369	·9337	·9304	·9273	·9240
760	·9479	·9446	·9414	·9381	·9349	·9316	·9286	·9252
761	·9492	·9459	·9426	·9394	·9362	·9329	·9298	·9264
762	·9504	·9471	·9438	·9406	·9374	·9341	·9310	·9276
763	·9517	·9484	·9451	·9418	·9387	·9353	·9322	·9289
764	·9529	·9496	·9463	·9431	·9399	·9365	·9334	·9301
765	·9542	·9509	·9475	·9443	·9411	·9378	·9347	·9313
766	·9554	·9521	·9488	·9455	·9424	·9390	·9359	·9325
767	·9567	·9533	·9500	·9468	·9436	·9402	·9371	·9337
768	·9579	·9545	·9512	·9480	·9448	·9414	·9383	·9349
769	·9592	·9558	·9525	·9492	·9460	·9427	·9395	·9362
770	·9604	·9571	·9538	·9505	·9472	·9439	·9408	·9374
771	·9617	·9583	·9550	·9517	·9485	·9451	·9420	·9386
772	·9629	·9595	·9562	·9529	·9497	·9463	·9432	·9398
773	·9642	·9608	·9575	·9542	·9509	·9476	·9444	·9410
774	·9654	·9620	·9587	·9554	·9522	·9488	·9456	·9422
775	·9667	·9632	·9600	·9566	·9534	·9500	·9469	·9435
776	·9679	·9644	·9613	·9579	·9546	·9512	·9481	·9447
777	·9692	·9657	·9625	·9591	·9559	·9525	·9493	·9459
778	·9704	·9670	·9638	·9603	·9571	·9537	·9505	·9471
779	·9717	·9682	·9650	·9615	·9582	·9549	·9517	·9483
780	·9729	·9695	·9662	·9628	·9595	·9562	·9530	·9496

779. Tension of Aqueous Vapour for each Tenth of a Degree Centigrade from 0° to 30° C. (*Regnault*).

Temp. C.	Tension in mm. of Mercury.	Temp. C.	Tension in mm. of Mercury.	Temp. C.	Tension in mm. of Mercury.	Temp. C.	Tension in mm. of Mercury.	Temp. C.	Tension in mm. of Mercury.
0·0	4·6	6·0	7·0	12·0	10·5	18·0	15·4	24·0	22·2
·1	4·6	·1	7·0	·1	10·5	·1	15·5	·1	22·3
·2	4·7	·2	7·1	·2	10·6	·2	15·6	·2	22·5
·3	4·7	·3	7·1	·3	10·7	·3	15·7	·3	22·6
·4	4·7	·4	7·2	·4	10·7	·4	15·7	·4	22·7
·5	4·8	·5	7·2	·5	10·8	·5	15·8	·5	22·9
·6	4·8	·6	7·3	·6	10·9	·6	15·9	·6	23·0
·7	4·8	·7	7·3	·7	10·9	·7	16·0	·7	23·1
·8	4·9	·8	7·4	·8	11·0	·8	16·1	·8	23·3
·9	4·9	·9	7·4	·9	11·1	·9	16·2	·9	23·4
1·0	4·9	7·0	7·5	13·0	11·2	19·0	16·3	25·0	23·5
·1	5·0	·1	7·5	·1	11·2	·1	16·4	·1	23·7
·2	5·0	·2	7·6	·2	11·3	·2	16·6	·2	23·8
·3	5·0	·3	7·6	·3	11·4	·3	16·7	·3	24·0
·4	5·1	·4	7·7	·4	11·5	·4	16·8	·4	24·1
·5	5·1	·5	7·8	·5	11·5	·5	16·9	·5	24·3
·6	5·2	·6	7·8	·6	11·6	·6	17·0	·6	24·4
·7	5·2	·7	7·9	·7	11·7	·7	17·1	·7	24·6
·8	5·2	·8	7·9	·8	11·8	·8	17·2	·8	24·7
·9	5·3	·9	8·0	·9	11·8	·9	17·3	·9	24·8
2·0	5·3	8·0	8·0	14·0	11·9	20·0	17·4	26·0	25·0
·1	5·3	·1	8·1	·1	12·0	·1	17·5	·1	25·1
·2	5·4	·2	8·1	·2	12·1	·2	17·6	·2	25·3
·3	5·4	·3	8·2	·3	12·1	·3	17·7	·3	25·4
·4	5·5	·4	8·2	·4	12·2	·4	17·8	·4	25·6
·5	5·5	·5	8·3	·5	12·3	·5	17·9	·5	25·7
·6	5·5	·6	8·3	·6	12·4	·6	18·0	·6	25·9
·7	5·6	·7	8·4	·7	12·5	·7	18·2	·7	26·0
·8	5·6	·8	8·5	·8	12·5	·8	18·3	·8	26·2
·9	5·6	·9	8·5	·9	12·6	·9	18·4	·9	26·4
3·0	5·7	9·0	8·6	15·0	12·7	21·0	18·5	27·0	26·5
·1	5·7	·1	8·6	·1	12·8	·1	18·6	·1	26·7
·2	5·8	·2	8·7	·2	12·9	·2	18·7	·2	26·8
·3	5·8	·3	8·7	·3	12·9	·3	18·8	·3	27·0
·4	5·8	·4	8·8	·4	13·0	·4	19·0	·4	27·1
·5	5·9	·5	8·9	·5	13·1	·5	19·1	·5	27·3
·6	5·9	·6	8·9	·6	13·2	·6	19·2	·6	27·5
·7	6·0	·7	9·0	·7	13·3	·7	19·3	·7	27·6
·8	6·0	·8	9·0	·8	13·4	·8	19·4	·8	27·8
·9	6·1	·9	9·1	·9	13·5	·9	19·5	·9	27·9
4·0	6·1	10·0	9·2	16·0	13·5	22·0	19·7	28·0	28·1
·1	6·1	·1	9·2	·1	13·6	·1	19·8	·1	28·3
·2	6·2	·2	9·3	·2	13·7	·2	19·9	·2	28·4
·3	6·2	·3	9·3	·3	13·8	·3	20·0	·3	28·6
·4	6·3	·4	9·4	·4	13·9	·4	20·1	·4	28·8
·5	6·3	·5	9·5	·5	14·0	·5	20·3	·5	28·9
·6	6·4	·6	9·5	·6	14·1	·6	20·4	·6	29·1
·7	6·4	·7	9·6	·7	14·2	·7	20·5	·7	29·3
·8	6·4	·8	9·7	·8	14·2	·8	20·6	·8	29·4
·9	6·5	·9	9·7	·9	14·3	·9	20·8	·9	29·6
5·0	6·5	11·0	9·8	17·0	14·4	23·0	20·9	29·0	29·8
·1	6·6	·1	9·9	·1	14·5	·1	21·0	·1	30·0
·2	6·6	·2	9·9	·2	14·6	·2	21·1	·2	30·1
·3	6·7	·3	10·0	·3	14·7	·3	21·3	·3	30·3
·4	6·7	·4	10·1	·4	14·8	·4	21·4	·4	30·5
·5	6·8	·5	10·1	·5	14·9	·5	21·5	·5	30·7
·6	6·8	·6	10·2	·6	15·0	·6	21·7	·6	30·8
·7	6·9	7	10·3	·7	15·1	·7	21·8	·7	31·0
·8	6·9	·8	10·3	·8	15·2	·8	21·9	·8	31·2
·9	7·0	·9	10·4	·9	15·3	·9	22·1	·9	31·4

THERMOMETRIC SCALES.

780. There are two different thermometric scales in use in this country, the Centigrade and Fahrenheit; the former of these is rapidly becoming universal for scientific purposes. The two scales are mutually convertible by the following formulæ, in which F.° represents a temperature on the Fahrenheit scale, C.° a temperature on the Centigrade scale:—

$$F^\circ = \frac{9\,C^\circ}{5} + 32$$

$$C^\circ = \frac{5\,(F^\circ - 32)}{9}$$

The temperatures referred to in this treatise are given on the Centigrade scale.

WEIGHTS AND MEASURES.

781. The corresponding values of the French and English weights and measures are given below. The use of the French or decimal system is strongly recommended by its extreme simplicity. The smaller denominations are obtained by taking a tenth, hundredth, thousandth, &c., of the unit chosen; they are designated by the Latin prefixes deci-, centi-, milli-, &c. The higher denominations are 10 times, 100 times, 1000, &c., times the unit, and are named by the Greek prefixes deca-, hecto-, kilo-, &c. Examples of this will be found in the Tables given below.

The starting-point of the French system is the "metre" (=39·37 inches); this is the "unit of length." The "unit of volume" is the "litre," which is 1 cubic decimetre. The "unit of weight" is the gram, which is the weight of 1 cubic centimetre of distilled water at 4° C.

The chief conveniences arising from the use of this system are:—

(1). That all the different denominations can be written as one; since they are either multiples by ten, or are decimal fractions, of the unit. Thus 5 decagrams, 3 grams, 4 decigrams, 8 milligrams would be written 53·408 grams.

(2). That since 1 cubic centimetre of water at 4° C. weighs 1 gram, we may obtain the *weight* of water in grams from its *measure*, by simply converting the measure into cubic centimetres. The number

thus obtained will represent at once the corresponding weight of water in grams. Of course this conversion is strictly accurate only when the water is measured at 4° C. But for ordinary purposes the error introduced, when the water is at the temperature of the air, is too small to be of any importance in the preparation of solutions. The necessary correction will be found in the Table (775).

The Weights and Measures which are most frequently used for chemical purposes are the gram, the millimetre (mm.), the litre, and the cubic centimetre (c.c.), which is $\frac{1}{1000}$ of a litre.

782. ENGLISH WEIGHTS AND MEASURES.

APOTHECARIES WEIGHT.

lb.		oz.		drms.		scruples.		grains.
1	=	12	=	96	=	288	=	5760
		1	=	8	=	24	=	480
				1	=	3	=	60
						1	=	20

AVOIRDUPOIS WEIGHT.

lb.		oz.		drms.		grains.
1	=	16	=	256	=	7000
		1	=	16	=	437·5
				1	=	27·343

IMPERIAL MEASURE.

gallon.		pints.		fluid oz.		fluid drms.
1	=	8	=	160	=	1280
		1	=	20	=	160
				1	=	8

1 gallon = 70,000 grains of water at 16°·7 C.
1 fluid ounce = $\frac{1}{20}$ pint = 437·5 ,, ,, ,,
1 gallon = 277·280 cubic inches.
1 fluid ounce = 1·733 ,,

783. FRENCH WEIGHTS AND MEASURES.

MEASURES OF LENGTH.

	metre.		inches.	ENGLISH. mile.	furlong.	yards.	feet.	inches.
Millimetre =	0·001	=	0·03937 =	.	.	.	.	0·03937
Centimetre =	0·01	=	0·39371 =	.	.	.	.	0·39371
Decimetre =	0·1	=	3·93708 =	.	.	.	.	3·9371
Metre =	1·0	=	39·37079 =	.	.	.	3	3·371
Decametre =	10·0	=	393·70790 =	.	.	10	2	9·7
Hectometre =	100·0	=	3937·07900 =	.	.	109	1	1
Kilometre =	1000·0	=	39370·79000 =	.	4	213	4	10·2
Myriometre =	10000·0	=	393707·90000 =	6	1	156	0	6

1 inch = 0·0254 metre = 2·5399 centimetres.
1 foot = 0·3048 ,,
1 sq. inch = 6·4514 sq. centimetres.

MEASURES OF CAPACITY.

1 litre = 1 cubic decimetre.

	litre.	cubic inches.	pints.
Millilitre, or Cubic centimetre (c.c.) =	0·001	= 0·06103	= 0·00176
Centilitre =	0·01	= 0·61027	= 0·01761
Decilitre =	0·1	= 6·1027	= 0·17608
Litre =	1·0	= 61·027	= 1·76077
Decalitre =	10·0	= 610·27	= 17·60773
Hectolitre =	100·0	= 6102·7	= 176·07734
Kilolitre =	1000·0	= 61027·0	= 1760·77341
Myriolitre =	10000·0	= 610270·0	= 17607·73414

1 cubic inch = 0·01639 litre.
1 cubic foot = 28·31531 litres.
1 gallon = 4·54336 ,,

MEASURES OF WEIGHT.

1 gram = the weight of 1 cubic centimetre (c.c.) of water at 4° C.

	grams.	grains.	Avoirdupois.
Milligram =	0·001	= 0·01543	
Centigram =	0·01	= 0·15432	
Decigram =	0·1	= 1·54323	
Gram =	1·0	= 15·43235	lbs. oz. drms.
Decagram =	10·0	= 154·32349	= 0 0 5·65
Hectogram =	100·0	= 1543·23488	= 0 3 8·5
Kilogram =	1000·0	= 15432·34880	= 2 3 5
Myriogram =	10000·0	= 154323·48800	= 22 1 2

1 grain = 0·0649 gram.
1 oz. (Troy) = 31·1035 grams.
1 lb. (Avoirdupois) = 453·593 ,,

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784. USEFUL MEMORANDA.

Weight of 1 c.c. of dry hydrogen at 0° C. and 760 mm. = 0·0000896 gram.

Weight of 1 c.c. of dry air at 0° C. and 760 mm. = 0·0012937 gram.

1 gram of hydrogen at 0° C. and 760 mm. measures 11·16 litres.

1 gram of air at 0° C. and 760 mm. measures 0·773 litre.

Specific gravity of hydrogen, air as unit, = 0·0693.

Specific gravity of air, hydrogen as unit, = 14·43.

Weight of 1 c.c. of mercury at 0° C. = 13·596 grams.

Coefficient of expansion for gases = $\frac{1}{273}$ = 0·003665.

Average percentage of oxygen in air, by volume, = 20·96.

SECTION II.

PREPARATION OF GASES.
DISTILLATION OF WATER.
LISTS OF APPARATUS AND CHEMICALS.

The Preparation of Gases.

785. Introductory Remarks.—Full descriptions will be found in Section VII. of *Clowes' Practical Chemistry* of the fitting and furnishing of the Chemical Laboratory, of the preparation of reagents and of reagent-bottles, and of methods of storage; descriptive lists of necessary chemicals and apparatus, and lists of chemical names with symbols and formulæ are also given. Reference to this Section will furnish all such general information.

786. A Convenient Form of Apparatus for furnishing a continuous stream of certain gases in a dry condition is shown in fig. 105. It is suitable for the preparation of any gas which is made by the action of a liquid upon a solid substance at ordinary temperature.

Two bottles (A, B), with tubulures near the bottom, are connected below by means of rubber tubing, as is shown in section in the figure. The bottle (A) contains the liquid, and is raised so as to deliver the liquid into the bottle (B), which contains the solid. The gas which is evolved is forced out by the pressure of the liquid in (A), and escapes through strong sulphuric acid, or some other purifying substance, which is contained in the bottle (C).

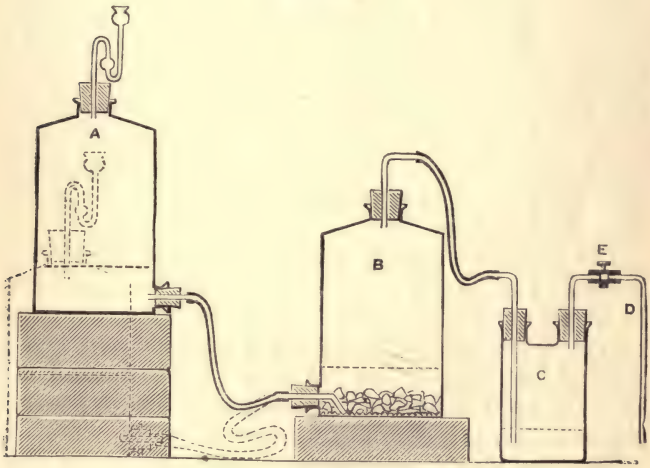
The escape of the gas can be regulated by adjusting the screw-clamp (E). When the clamp is closed, the pressure of the gas collecting in (B) forces back the liquid into (A), and

stops the further generation of the gas. The production of gas recommences as soon as the clamp is opened, since the liquid flows once more into (B) as soon as the gas is allowed to escape, and its pressure is thus reduced.

When the apparatus is not in use, the vessel (A) is lowered so as to take off all unnecessary pressure: it is shown in this position in dotted outline in the figure.

It is well to introduce a layer, an inch in depth, of roughly broken glass into (B), so as to prevent the solid from remaining in contact with acid at the bottom of the bottle when the apparatus is not in use. Rubber corks are used, and are fastened down by wire to the necks and tubulures of the bottles.

FIG. 105.



In Preparing the Following Gases, the materials specified below should be used:—

Hydrogen; zinc and dilute sulphuric or hydrochloric acid.

Carbon dioxide; marble and dilute hydrochloric acid.

Hydrogen sulphide; ferrous sulphide and dilute hydrochloric or sulphuric acid.

The Distillation of Water.

787. The Process of Distillation may be carried on in the constant still figured and described below. The sketch in fig. 106 renders a lengthened description unnecessary. It represents the apparatus in section and about one-twentieth its working size, with the exception of the side-feed to the boiler, which is about twice its real diameter.

The water in a copper still (A) is heated by the flame of a Fletcher-burner or of a large-sized Bunsen-burner. The steam thus generated passes from the top of the still through a spiral block-tin tube immersed in water in the condensing-tub (B), which is made of copper or of galvanised iron. From this condenser the distilled water flows into a large stone-ware vessel (C), which is furnished with a tap below, from which the water is drawn when required. A long syphon tube (CD) serves as a gauge to indicate the level of the water inside the jar.

The condensing-tub (B) is constantly supplied with cold water from a tap (G) which feeds through the funnel-tube to the bottom of the condenser. The overflowing hot water runs from the tube (H) at the top of the condenser into a side-feed for supplying the boiler. From the side-feed the excess of water flows down a central tube through a waste-pipe to a sink, as is shown by the arrow.

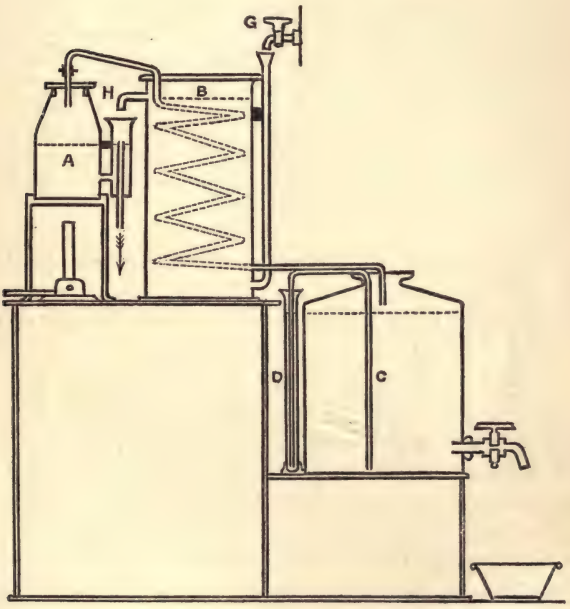
The spiral block-tin pipe in the condenser must be of sufficient diameter to prevent it from offering any obstruction to the free escape of the steam from the boiler. Every part of it must have a downward slope in order to prevent water from collecting in it: and the coils must be supported in position by a suitable framework of wood or metal to prevent them from sinking.

The copper still should be furnished with a broad lid screwing upon its mouth, for convenience in removing the deposit which collects within. Into this lid should be fastened a brass tube carrying a screw-union, by which the tin condensing-pipe may be connected steam-tight with the still.

By the above arrangement the boiler is constantly supplied with the hottest water from the condenser through the side-feed: and the water in the boiler is always maintained at the level shown by the dotted line.

As soon as the apparatus has been properly fitted up and the supply of water has been duly adjusted, it is only neces-

Fig. 106.



Scale $\frac{1}{20}$

sary to light and extinguish the gas under the still when the distillation is started and stopped. It is advisable to remove occasionally the incrustation from the interior of the still, and from the supply-tube for hot water from the condensing vessel.

The wooden stand for the still and the storage-jar is

conveniently fitted with shelves and doors to serve as a store-closet.

Such a copper still, 23 inches in circumference below and 8 inches in height, when filled to a height of 4 inches and heated by a large Bunsen-burner, yields about 2 litres of distilled water per hour.

Another form of still, combined with steam-ovens, is described in par. **39**.

In laboratories which require a larger supply of distilled water than can be furnished by the above apparatus, a copper still of several gallons capacity may be set in masonry and heated by a small furnace fed with coal, coke, or gas. The overflow from the condenser should then pass into a small cistern, the overflow-pipe of which keeps its water surface level with that required in the still. The still is supplied with hot water, by connecting it with this cistern by means of a tube bent downwards in its middle, so as to hinder the circulation of water between the still and the cistern.

788. Pure Distilled Water free from Organic Matter.—If the distilled water which is used in the Permanganate Process (**538**) is not known to be free from organic matter, it should be treated in the following way.

About 1 gram of potassium hydrate and 0·2 gram of potassium permanganate are added to about 5 litres of distilled water in the distillation flask (**532**), which is fitted with a reflux condenser. The liquid is gently boiled for twenty-four hours, and is then distilled into Nessler cylinders (**531**) as long as the distillate gives any colour with Nessler solution (**530**). The distillate, which is now free from ammonia and organic matter, is received in a clean Winchester quart-bottle.

List of Apparatus Required.

The following apparatus will be required for Quantitative Analysis, in addition to that usually provided for Qualitative Analysis; see *Clowes' Qualitative Analysis* (1000–1012).

The numbers in parentheses refer to paragraphs in the preceding text.

789. Apparatus for Each Student.

Parts I. and II.—Gravimetric.

Weighing-bottle (16).
Pair of watch-glasses, 2 inches in diameter, with clip (16).
Desiccator (fig. 25, p. 37).
Beakers; two 8 oz.; two 16 oz.
Quantitative filter-papers; 3½ and 4½ inches in diameter. Schleicher and Schüll's are recommended (53, 57, 63).
Three funnels, with ground edges.
Two porcelain crucibles, 1½ and 1¾ inches in diameter.
Two porcelain dishes, 4 inches in diameter.
Two clock-glasses, 4 inches in diameter.
Piece of platinum wire, 8 inches in length.

790. Apparatus for General Use.

Apparatus marked with an asterisk will only serve for five or six students. If it is inclosed in brackets it is not indispensable.

Parts I. and II.—Gravimetric.

*A balance (1). No. 10, of Becker's, Rotterdam, serves well.
*A box of brass and aluminium weights, with several 12 milligram riders (4).
Specific-gravity bottle, 50 grams capacity (24, 25).
Sprengel tube (26, 27).
Hydrometers (28).
*Two Centigrade thermometers, graduated on the stem; one from 10° to 100°, the other from 0° to 300°.
Fractionating-flasks of 6 oz., 10 oz., and 70 oz. capacity (31, 532). The largest size must be fitted with a ground glass stopper.
Steel percussion mortar (35).
Porous tiles (80).
Iron mortar, 8 inches in diameter.
Air-oven (40).
Air-bath (50, *d*).
Beakers, 32 oz. capacity.
Sieves of brass wire (35, 142).

Porcelain dishes, 8 inches in diameter.
Round flask, 20 oz. (255).
Funnels, 6 inches in diameter.
Large desiccator (p. 38).
Rose's crucible, or substitute (67).
Iron plate on feet (p. 45).
*Platinum crucible, 1 inch high and across, about 16 grams in weight (65).
Nickel crucibles, 1¾ inches in diameter.
Platinum dish, 3½ inches in diameter.
Silver dish, 3½ inches in diameter.
Nickel dish, 4 inches in diameter.
Geissler-pump (58).
Filter-flask (p. 54).
Hot-water funnel jacket (p. 71).
Filters, 10 inches, cut.
*U-tubes of various shapes (142, 143, 295).
Calcium chloride tubes, straight, 4 inches.
*Liebig's or Geissler's potash-bulbs (140, 650).
50 c.c. pipettes, ungraduated.
Two 10-oz. conical flasks.
[Schrötter's carbonic acid apparatus (147).]
Straight bulb-tube (p. 128).
Combustion tubing, mainly five-eighth inch in internal diameter; some 1 inch in diameter.
Porcelain boat, small and large (158, 456, 646).

Parts III. and IV.—Volumetric and General.

*Measuring-flasks; 1000, 500, 250, 200, 100 c.c. capacity (208).
*Pipettes; 50, 25, 20, 10, and 5 c.c. capacity (214).
Pipette, 10 c.c. graduated into tenths of a c.c. (214).
*Mohr's burettes, 50 c.c. capacity graduated into tenths of c.c.; one with glass stopcock below (216).
*Measuring-cylinders, graduated throughout; 1000, 500, 250, and 100 c.c. capacity (219).
[Erdmann's float (fig. 68, p. 158).]
[Weight burette (242).]
Thompson's calorimeter (479).
Six Nessler-cylinders, 6 inches in height, 1½ inches in diameter, about 100 c.c. capacity (531).
Microscope, with one-sixth objective.
Schmid's milk-tube (fig. 77, p. 347).
Soxhlet's extractor (589).
Butter-flask (fig. 79, p. 360).

[Alcohol still for beer (fig. 80, p. 365).]
Hydrometer (28).
Erlenmeyer's combustion-furnace, 26 inches in length.
Copper-gauze.
Silver-gauze.
Calcium chloride U-tubes (649).
Nitrogen bulbs, Will and Varrentrap's (fig. 86, p. 404).
Digester for sealed tubes (fig. 89, p. 417).
Raoult's apparatus (fig. 90, p. 424).
Thermometer, showing hundredths of degrees.

Assaying.

Cupels.
Cupel-mould.
Conical mould.
Assay-tongs.
Gas muffle-furnace.
Wind-furnace.
Crucibles, wrought-iron and clay.

Part V.—Gas Analysis.

The Hempel apparatus and pipettes (692).
[The Winkler burette (697).]
The Lunge nitrometer (714).
[The Scheibler apparatus (725).]
Graduated gas-tubes 50, 100, 200 c.c.
Bottle for air-sample (732, *a*).
The Meyer apparatus (737).
[The Dumas apparatus (740).]
[The Russell and West apparatus (728).]

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791. List of Chemical Reagents Required.

This list is supplementary to the lists already given for Qualitative Analysis (1035–1048) in *Clowes' Practical Chemistry*. The references are to descriptions of preparation.

Fuming nitric acid, 1·5 sp. gr.
Sodium peroxide (104).
Bromine (103).
Lead nitrite (121).
Magnesia-mixture (132).
Soda-lime (142).
Pumice.
Litmus (223).
Cochineal (225).
Turmeric (226).
Methyl-orange (227).
Phenol-phthalein (228).
Sodium.
Steel pianoforte wire.
Ferrous ammonium sulphate (81, *c*).
Ammonium bisulphite.
Potassium permanganate, crystals.
Iodine (83).

Starch-solution (278).
Sodium sulphide (307).
Glacial acetic acid.
Uranium nitrate.
Tricalcium phosphate.
Neutral potassium oxalate.
Ammonium acetate.
Ammonium molybdate solution (449).
Chromic anhydride (455).
Copper ammonium chloride (81).
Bone-ash (498).
Sheet lead, free from silver.
Pure silver.
Argol, or crude tartar.
Red lead.
Flour.
Nessler-solution (528).
Metaphenylene-diamine (540, *a*).
Silver nitrite (540, *c*).
Emplastrum plumbi (*B.P.*) (546, *b*).
Soap-solution (546, *b*).
Sheet-lead strips.
Ether (585).
Fehling-solution (610).
Chloroform.
Hide-powder (621).
Indigo-carmine, pure (622, *b*).
Gelatin (Nelson's).
Kaolin.
Absolute alcohol.
Petroleum ether.
Copper oxide, by oxidation.
Asbestos.
Mercuric oxide, precipitated.
Pyrogallic acid.
Cuprous chloride solution (698, *c*).
Palladium.
Hydrogen peroxide, 10 per cent. solution (723).
Calcined magnesia.
Resin cerate.
Mercury, free from foreign metals.

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792. List of Substances for Experiments and Analysis.

Note.—All salts marked (*) are purified by recrystallisation (79).

Iceland-spar.
Sugar-candy.
Petroleum.
*Potassium chlorate.
*Copper sulphate.
*Alum.
*Nickel ammonium sulphate.
*Ferrous ammonium sulphate.
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